COO-1198-1246

MASTER

MASTER

STUDIES IN THE ELECTRONIC STRUCTURE OF MATTER

BY

DONALD LYNN MILLER

B.S., University of Missouri, 1973
M.S., University of Illinois, 1974

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Physics
in the Graduate College of the
University of Illinois at Urbana-Champaign, 1979

Urbana, Illinois

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

STUDIES IN THE ELECTRONIC STRUCTURE OF MATTER

BY

DONALD LYNN MILLER

B.S., University of Missouri, 1973
M.S., University of Illinois, 1974

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Physics
in the Graduate College of the
University of Illinois at Urbana-Champaign, 1979

Urbana, Illinois

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

STUDIES IN THE ELECTRONIC STURCTURE OF MATTER

Donald Lynn Miller, Ph.D.
Department of Physics
University of Illinois at Urbana-Champaign, 1979

CHAPTER ONE: KLL Auger transition rates for helium are computed using simple atomic orbital wavefunctions which take into account the difference in average electron-electron repulsion of initial and final states. The results are consistent with transition rates computed by other authors using a variety of many-electron techniques. It is suggested that wavefunctions determined in the manner described provide a useful representation of the autoionizing state within the first Bohr radius.

CHAPTER TWO: A method for extracting atomic pseudopotentials from photoelectron angular distributions is described and applied photoionization of the outermost p shells of Ar, Kr, and Xe and to the 4d shell of Xe. The pseudopotentials obtained reproduce the data, and also predict accurate cross sections and phase shifts for photoelectron energies up to 100 eV. It is suggested that the pseudopotentials aptly mimic the effects of intrashell electron-electron correlations in the photoionization process.

CHAPTER THREE: The extended Hückel theory is applied to the nitrogen trap in GaAs and GaP. Perfect crystal band structures are computed and are shown to be in reasonable agreement with those computed with empirical pseudopotentials. Nitrogen impurity levels in GaAs and GaP are computed using an extended Hückel cluster model. In each case the model predicts two states within the band gap, in constrast to experi-

ment which detects one impurity state in GaP and none in GaAs. It is suggested that the choice of cluster used unrealistically concentrates states near the conduction band edge on the central atom.

ACKNOWLEDGEMENTS

I would like to thank Professor John D. Dow for his guidance and encouragement during the course of this work.

I am especially indebted to Don Franceschetti for his collaboration on the calculation of autoionization lifetimes, and to Coenraad Swarts for collaboration on the extended Hückel calculations.

I thank my colleagues H. Hjalmarson, P. Vogl, and C. Myles for sharing successes and setbacks.

Special thanks go to J. Burke for contributing to innumerable stimulating discussions.

I am pleased to acknowledge the friendship of K. E. Schmidt, P. T. Cahill, and L. C. Rathbun, and the comradarie of the intramural sports teams, which have made my years in Urbana much more pleasant.

I thank Pat Coombs for her patient and excellent work in typing this thesis.

I thank my family for their support, especially my parents who are my first and most perservering teachers.

My deepest appreciation is reserved for my wife, Peggy, who has given me constant love and support, and Erin.

Finally, I am pleased to acknowledge support in the forms of National Science Foundation, H. J. Diffenbaugh, and U. S. Steel Foundation Fellowships; NSF grants GH 33634 and DMR 720 3026; U.S. ERDA Grant EY-76-C-02-1198; and U.S. Navy contract N00014-77-C-0537; as well as support from the University of Illinois.

PREFACE

This thesis deals with three distinct problems in electronic structure, with a single unifying aspect. Each chapter documents the application of a simple, almost intuitive, approach to a system which would normally be treated only by more complex methods. Each chapter is self contained, including figures, references, and equations.

The material of Chapter One has been previously published: D. L. Miller and D. R. Franceschetti, J. Phys. B 9, 1471 (1976). Portions of the material of Chapter Two have also been published: D. L. Miller and J. D. Dow, Phys. Lett. 60A, 16 (1977); and D. L. Miller, J. D. Dow, R. G. Houlgate, G. V. Marr, and J. B. West, J. Phys. B 10, 3205 (1977).

TABLE OF CONTENTS

CHAPTER ONE: A SIMPLIFIED CALCULATION OF AUTOIONIZATION RATES FOR DOUBLY EXCITED STATES OF HELIUM 1

I. INTRODUCTION 2

II. METHOD 5

III. DISCUSSION 8

IV. SUMMARY 13

REFERENCES 14

CHAPTER TWO: ATOMIC PSEUDOPOTENTIALS FOR PHOTOIONIZATION OF RARE GASES 16

I. INTRODUCTION 17

II. UNITS 20

III. METHOD 21

IV. RESULTS 34

A. Argon 34
B. Krypton and Xenon 49
C. Continuum Phase Shifts, Quantum Defects, and Dipole Matrix Elements 49
D. Intershell Effects in Xenon 66

V. CONCLUSIONS 80

APPENDICES:

A. DIPOLE SUM RULES 82
B. THEORY OF PHOTOIONIZATION 89
C. INTERSHELL CORRELATIONS 96
D. LISTING OF PHOTOIONIZATIONS PROGRAMS 103

1. Sample main program 104
2. Subroutines for calculating asymmetry parameters and cross sections 107
3. Subroutine for calculating Coulomb functions. 124

REFERENCES 133

CHAPTER THREE: EXTENDED HÜCKEL THEORY OF THE NITROGEN TRAP IN GALLIUM ARSENIDE PHOSPHIDE 135

I. INTRODUCTION 136

II. METHOD 138

A. The Extended Hückel Hamiltonian 138
B. Perfect Crystals 139
C. Cluster Model 140
D. Periodic Impurities 141

III. CALCULATIONS 142

A. Band Structures 142
B. Cluster Calculations 145

IV. CONCLUSIONS 154

APPENDICES:

A. MULLIKEN POPULATION ANALYSIS 159
B. CONSTRUCTION SYMMETRY ORBITALS 162

1. Method 162
2. Irreducible Representations of T_d 164

a. Group Elements 164
b. Irreducible Representations 167

C. EXTENDED HÜCKEL PROGRAMS 171

1. Program to group equivalent pairs of atoms... 172
2. Program to calculate overlap matrix 176
3. Program to calculate energy levels and eigenvectors 197

REFERENCES 206

VITA 207

CHAPTER ONE:

A SIMPLIFIED CALCULATION OF AUTOIONIZATION RATES FOR DOUBLY EXCITED STATES OF HELIUM

I. INTRODUCTION

The Auger effect, the decay of an atomic inner shell vacancy state by autoionization, has been understood in principle for some time[1]. Although a substantial literature concerning the phenomenon now exists[2,3], our understanding of autoionization in even the simplest atomic systems is far from complete. Recent developments in the field include the efforts of a number of authors[4-12] to compute autoionization transition rates for doubly excited helium atoms, taking full account of the electron-electron interaction. The results of these calculations are significant for at least two reasons: (i) With only two electrons, the helium atom provides the simplest system available for the study of electron-electron correlation effects on any physical property. In view of the rapid increase in computational complexity with the number of electrons, it is quite likely that qualitative information gained from extensive calculations on helium will be applied to more complex systems before calculations of comparable accuracy are attempted. (ii) The existence of high accuracy calculations for He permits the testing and refinement of simpler approximate methods more directly related to physical intuition. This chapter reports the test of one such method. Although it neglects instantaneous electron-electron correlations, the method is shown to provide reasonable autoionization linewidths for helium. Its primary utility, however, derives from its direct applicability to the singly and multiply

excited states of other low Z atoms and ions since most of these have not been studied by many body methods.

Our approach employs an independent electron model in which wavefunctions are written as Slater determinants (or a simple linear combination thereof as required by symmetry) of atomic orbitals. Our method is based on the realization that the effective one-electron Hamiltonian (Fock operator[13]) whose eigenfunctions provide the best single determinant approximation to the wavefunction of a given state is unique to that state since it explicitly contains the averaged electron-electron repulsion of that particular state. Thus by determining initial and final state wavefunctions in independent calculations we are able to take into account the averaged electron-electron repulsion appropriate to each state.

We believe it useful to distinguish between this averaged repulsion, which might be obtained in an independent self-consistent single determinant calculation for each state, and the instantaneous correlation of electron motion which is included only in a full many-body treatment. Since some many-body methods (at least implicitly) expand all N-electron wavefunctions in terms of the same set of atomic orbitals, it may be difficult in such cases to differentiate between the two effects. The present calculation was undertaken in part to permit such a separation in the case of helium autoionization.

Earlier and more rudimentary calculations[14,15] have shown that in three-electron atoms the type of effect discussed here is an important factor in determining the rate of autoionization. The results presented here permit us to gauge the reliability of such calculations and provide guidance in approaching autoionization in other few electron systems.

II. METHOD

The Auger transition rate is given in atomic units ($e = \hbar = m_e = 1$; energy unit = 2Ry) by the well-known "golden rule" formula

$$W = 2\pi \left| \langle f | \frac{1}{r_{12}} | i \rangle \right|^2 \rho_f(E). \tag{1}$$

The initial state $|i\rangle$ involves an empty 1s shell and the final state $|f\rangle$ includes a continuum electron. We have determined initial and final state wavefunctions for all possible KLL Auger transitions by independent variational calculations.

The final state wavefunctions were taken to be of the form:

$$|f\rangle = \frac{1}{2}[\phi(1)\chi(2) \pm \chi(1)\phi(2)][\alpha(1)\beta(2) \mp \beta(1)\alpha(2)] \tag{2}$$

with signs chosen appropriately for singlet and triplet states. ϕ was taken to be a hydrogenic 1s function, as appropriate for the residual He^+ ion, while the continuum function was determined by solving[16]

$$(H_0 - \tfrac{1}{2}k^2 + J \mp K)\chi = \mp\langle\phi|H_0 - \tfrac{1}{2}k^2|\chi\rangle\phi, \tag{3}$$

where

$$H_0 = \frac{-\nabla^2}{2} - \frac{Z}{r} \tag{4}$$

is the hydrogenic Hamiltonian, $\frac{1}{2}k^2$ is the energy of the continuum electron,

$$J\chi(r_1) = [\int d^3r_2|\phi(r_2)|^2 r_{12}^{-1}]\chi(r_1) \tag{5}$$

and

$$K\chi(r_1) = [\int d^3r_2\phi^*(r_2)\chi(r_2)r_{12}^{-1}]\phi(r_1) \tag{6}$$

define the direct and exchange Coulomb operators.

An iterative series of Numerov integrations[17/] was performed to provide self-consistent, numerical solutions of Equation (3).

As mentioned above, the initial states were taken to be Slater determinants, or a linear combination thereof, as required in the LS coupling scheme. The independent electron orbitals used were of the form

$$\psi_{2s} = N_{2s}[re^{-\zeta_1 r} - \lambda e^{-\zeta_2 r}]Y_{0,0}(\theta,\phi), \tag{7a}$$

$$\psi_{2p} = N_{2p}re^{-\zeta_3 r}Y_{1,m}(\theta,\phi) \tag{7b}$$

with $\zeta_1, \zeta_2, \zeta_3$ being the variational parameters[18/]. A separate variational calculation was performed for each LS term. In addition, configuration mixing of the $2s^2$ and $2p^2$ ^1S states

was determined by diagonalization of the Coulomb operator. In calculations involving 2s orbitals, the parameter λ was constrained to maintain orthogonality to the final state 1s orbital. This procedure provides physically reasonable wavefunctions with the assurance that the autoionizing states are approximately orthogonal to all lower lying states.

It should be noted that our method falls within the framework of Feshbach's "Q-operator" formalism[19,20]. Within this framework, our autoionization widths are an approximation to the true value. Our energies, however, should be viewed as approximations to the eigenvalues, ε_λ of the operator QHQ where

$$Q = (1-|\phi(1)\rangle\langle\phi(1)|)(1-|\phi(2)\rangle\langle\phi(2)|). \qquad (8)$$

These eigenvalues differ from the true positions, E_λ by an amount Δ_λ which has been shown by other authors to be small.[11]

III. DISCUSSION

Included in Table I are the results of a number of recent calculations: Propin's[4] four term C.I. with screened hydrogenic wavefunctions, Herrick's[5-7] C.I. calculation using a much larger, but unscreened, hydrogenic basis, the close coupling scattering theoretic calculations of Burke *et al.* [8,9], and the calculation of Bhatia and Temkin, who employed a Hylleraas-type variational function within the projection operator formalism[10-12]. The latter provides the closest agreement with experiment[21-25] achieved to date, owing in part to the explicit appearance of r_{12} in the trial function, which allows a particularly accurate approximation to electron-electron correlation.

Examining the calculated energies, we find that our results, including $2s^2$-$2p^2$ configuration interaction, agree with the experimental values within 2%. All of the other theoretical calculations included, however, achieve somewhat better agreement with experiment. It is often stated that the autoionization width is quite sensitive to the detailed nature of the atomic wavefunction[2]. A striking confirmation of this statement is found on comparing the results of Herrick[5] and Propin[4]. Although the initial state energies obtained by the two authors agree within 0.2% and their final state wavefunctions are of the same form, their calculated linewidths disagree by as much as 50%. Our autoionization widths are in considerably better agreement with the results of the most detailed calculations[10-12] than those of Propin[4] and agree nearly as well as those of Herrick[5].

The only disappointing result of our calculation is the very small width for the $2p^2\ ^1S$ state. The Auger matrix element in this case involves the difference of nearly equal quantities and thus is extremely sensitive to small inaccuracies in the atomic wavefunctions. It should also be noted that there is little agreement among previous calculations of this width.

The agreement observed between our calculated Auger widths and those obtained in far more detailed calculations leads us to believe that the essential physical factors determining the Auger transition rate are well represented in our wavefunctions. This is at first surprising since our independent electron wavefunctions, obtained in simple variational calculations, are not even self-consistent solutions of the Hartree-Fock equations. We argue, however, that (i) the self-consistent solution of the Hartree-Fock equation is a particularly good approximation to the true wavefunction for most of the doubly excited states considered, (ii) our variational calculations produce wavefunctions which closely approximate the self-consistent wavefunctions in the inner shell region, and (iii) the behavior of the wavefunction in the inner shell region is the most important factor determining the Auger transition rate.

The dominant contribution to the energy of a doubly excited state is the electron-nucleus attraction. (Note that this contribution is proportional to $\langle r^{-1}\rangle$ while the electron-electron repulsion contribution is roughly proportional to $1/\langle r^2\rangle$.) Starting with the best independent electron approximation to the $2\ell 2\ell'\ ^{2S+1}L$ state, one expects only small configuration interaction admixtures of higher $n\ell''n'\ell'''\ ^{2S+1}L$

Table I. Energies (above ground state) and autionization widths for doubly excited states of Helium.

Energy (eV)					
$2s^2\,^1S$	$2s2p\,^3P$	$2s2P\,^1P$	$2p^2\,^1S$	$2p^2\,^1D$	Source
59.42	58.49	61.10	62.31	60.93	This calculation (one configuration)
57.90	---	---	63.83	---	This calculation (two term C.I.)
57.99	58.44	60.37	62.75	60.19	Propin[4/]
57.92	58.39	60.33	62.78	60.09	Herrick[5-7/]
57.86	58.36	60.27	62.81	60.02	Burke *et. al.*[8,9/]
57.84	58.32	60.15	62.09	59.91	Bhatia *et. al.*[10-12/]
57.82[a]	58.34[a]	60.12[b]	62.15[a]	59.95[c]	Expt.

Autionization Width (eV)					
$2s^2\,^1S$	$2s2p\,^3P$	$2s2P\,^1P$	$2p^2\,^1S$	$2p^2\,^1D$	Source
0.091	0.018	0.032	0.049	0.105	This calculation (one configuration)
0.149	---	---	0.00095	---	This calculation (two term C.I.)
0.221	0.033	0.024	0.004	0.087	Propin[4/]
0.14	0.022	0.036	0.0077	0.082	Herrick[5-7/]
0.14	0.011	0.044	0.019	0.073	Burke *et al.*[8,9/]
0.125	0.0089	0.036	0.0067	0.073	Bhatia *et al.*[10-12/]
0.138 ±.015[d]	0.0094 ±.0006[e]	0.038 ±.004[b]	---	0.072 ±.018[d]	Expt.

[a] Ref. 25 [b] Ref. 24 [c] Ref. 22 [d] Ref. 23 [e] Ref. 21

states (n or $n' > 2$) since those admixtures reduce electron-electron repulsion only at the cost of increasing the electron nucleus separation. For the transitions considered here, one therefore need only be concerned with the interaction of the $2s^2$ and $2p^2\ {}^1S$ states, since those states correspond to nearly equal values of $\langle r^{-1}\rangle$ and their interaction permits electron correlation without increasing the electron nucleus separation.

The largest contribution to $\langle r^{-1}\rangle$ arise from the region of the atom within the first Bohr radius. Since $\langle r^{-1}\rangle$ determines the greater part of the total energy, a variational calculation will provide a good apprximation to the wave function in that region, even at the expense of an accurate description of the wavefunction in other regions, provided that the trial function provides sufficient flexibility. We note that a trial function with variable exponents (Eq. (7)) is particularly suitable in this respect.

Cooper[25/] and Fano and Cooper[27/] have pointed out that despite the long range nature of the Coulomb interaction, the dominant contribution to the Auger matrix element

$$\int d^3r_1 \int d^3r_2 \psi_f^*(r_1,r_2)\frac{1}{r_{12}}\psi_i(r_1,r_2) \qquad (9)$$

arises from the region in which both electrons are near the nucleus. Since ψ_f involves a 1s electron, the dominant contribution to this matrix element arises from the region of configuration space in which both electrons are near the nucleus, for in that region both ψ_f and r_{12}^{-1} will be large. Thus

the initial state wavefunctions employed in our calculation, although simple in form, permit a close approximation to the actual transition rate.

IV. SUMMARY

We have presented a simple method for the calculation of KLL Auger transition rates of low Z atoms and ions. Wavefunctions employed are single Slater determinants (or simple linear combinations) and initial and final states are determined in independent variational calculations. The method is based on the realization that the average electron-electron repulsion may differ considerably in initial and final states.

KLL decay rates were computed for doubly excited helium and compared with the results of experiment and high-accuracy calculations. The results suggest that the autionization width may be reliably estimated without taking into account the instantaneous correlation of electron motion. It is reasonable to expect that similar physical considerations govern the decay of single and double K shell vacancies in other low Z atoms. Calculations of the autionization width in such systems using the method described should distinguish between long-lived and short-lived states and should predict the width of the latter to within a factor of 2.

It is only a matter of time before high accuracy configuration interaction calculations are available for the autionization of atoms with more than two electrons. We feel, however, that simple, physically inspired methods will remain valuable both in sorting out experimental data and in advancing our conceptual understanding of the autionization process.

REFERENCES

1. G. Wentzel, Z. Physik 43. 524, (1927).

2. W. Bambynek, B. Craseman, R. W. Fink, H.-U. Freund, H. Mark, C. D. Swift, R. E. Price and P. V. Rao, Rev. Mod. Phys. 44, 716 (1972).

3. E. H. S. Burhop and W. N. Asaad, Advances in Atomic and Molecular Physics, ed. D. R. Bates (Academic Press, New York, 1972), Vol. 8, p. 164.

4. R. Kh. Propin, Optics and Spectroscopy 8, 158 (1960).

5. D. R. Herrick, Ph.D. Thesis, Yale University (1973).

6. D. R. Herrick and O. Sinanoglu, Phys. Rev. A11, 97 (1975).

7. O. Sinanoglu, and D. R. Herrick, J. Chem. Phys. 62, 886 (1975).

8. P. G. Burke and D. D. McVicar, Proc. Phys. Soc. 86, 989 (1965).

9. J. W. Cooper, S. Ormonde, C. H. Humphrey, and P. G. Burke, Proc. Phys. Soc. 91, 285 (1967).

10. A. K. Bhatia, A. Temkin, and J. F. Perkins, Phys. Rev. 153, 177 (1967).

11. A. K. Bhatia and A. Temkin, Phys. Rev. 182, 15 (1969); and Phys. Rev. A11, 2018 (1975).

12. A. K. Bhatia, Phys. Rev. A6, 120 (1972).

13. V. Fock, Z. Phyzik 61, 126 (1930).

14. D. R. Franceschetti, Proc. 4th Int. Conf. on Vacuum Ultraviolet Radiation Physics, eds. E. E. Koch, R. Haensel, and C. Kunz (Permagon Press, New York, 1974), p. 663.

15. D. R. Franceschetti and J. D. Dow, J. Phys. F4, L151 (1974).

16. P. M. Morse and W. P. Allis, Phys; Rev. 44, 269 (1933).

17. J. M. Blatt, J. Comp. Phys. 1,382 (1967).

18. P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. 48, 948 (1935).

19. H. Feshbach, Ann. Phys. (N.Y.) 5, 357 (1958); and Ann. Phys. (N.Y.) 19, 287 (1962).

20. S. Geltman, Topics in Atomic Collision Theory (Academic Press, New York, 1969), p. 142.

21. H. G. Berry, J. Desesquelles and M. Dufay, Phys. Rev. A6, 600 (1972).

22. P. D. Burrow, Phys, Rev. A2, 1774 (1970).

23. P. J. Hicks and J. Comer, J. Phys. B8, 1866 (1975).

24. R. P. Madden and K. Codling, Astrophysical J. 141, 364 (1965).

25. M. Rudd, Phys. Rev. Lett. 15, 580 (1965).

26. J. W. Cooper, Atomic Collision Processes, (North-Holland, Amsterdam, 1964), p. 595.

27. U. Fano and J. W. Cooper, Phys. Rev. 137, A1364 (1965).

CHAPTER TWO:

ATOMIC PSEUDOPOTENTIALS FOR PHOTOIONIZATION OF RARE GASES

I. INTRODUCTION

The angular distributions of photoemitted electrons hold some promise of being useful in the identification of adsorbates and in determining their orientation on solid surfaces. It seems desirable then to be able to analyze such distributions as quickly, efficiently, and accurately as possible.

As a first step in this direction, we have considered the photoionization properties of single atoms, and have found in even the simplest cases (i.e. rare gas atoms) that the standard theories leave something to be desired.[1/]

Local density methods such as the Hohenberg-Kohn-Sham[2-3/] and X_α[4/] calculations, are easily applied and efficient. However, their ability to describe such basic properties as the photoionization cross section and photoelectron angular distribution ranges from inadequate to terrible, depending upon the prescription used for the local potential.

Hartree-Fock (HF) calculations[5/] require more computation than the local density methods; but, the effort involved is still reasonable. This method also provides accurate ground state properties, i.e. orbital energies and wavefunctions. In fact, this method provides the best possible single determinant wavefunction for the ground state. However, it is not reliable when used to calculate continuum properties. As examples of this we note that the f-sum rule is not satisfied in this approach (see appendix A and reference 5) and that it fails

to produce accurate values for cross sections and angular distributions.

The most accurate calculations to date are those of Amusia and co-workers using the Random Phase Approximation with Exchange (RPAE).[6-9] This method, which is equivalent to time-dependent HF theory[7], uses a many electron, diagramatic, approach to include the effects of dynamic correlations. Typically, RPAE cross sections agree with experiment to within 5-10%, and computed angular distributions are reasonable. Furthermore, by including an infinite class of diagrams, the RPAE avoids the sum rule problems that plague HF calculations. The principal drawback of this approach is its computational complexity, which renders similar calculations for larger systems intractable.

As an alternative to these *à priori* methods we have proposed[10] that the continuum properties of photoionization may be described by a local, static pseudopotential, which may be extracted from experimental data. The method is conceptually simple. Photon absorption is treated as a one-electron process, so long as dynamic effects are dominated by a single subshell of electrons. If necessary, intershell effects may be included by second order perturbation theory. The method is fast. The amount of computation required is comparable to that used in a HF calculation and is significantly less than that required by the RPAE. The method is also accurate. We shall show that it is much more reliable

than either HF or local density calculations, and compares favorably to the RPAE.

II. UNITS

In this chapter we take advantage of the atomic system of units to simplify the equations. In this system $\hbar = m_e = e = 1$, where m_e and e are the mass and charge of an electron. The unit of length is the hydrogenic Bohr radius and the unit of energy is the Hartree (1 Hartree = 2 Rydbergs).

III. METHOD

Since we are interested in a local pseudopotential which completely characterizes the scattering properties of an atom, and we wish to fix this potential using experimental measurements, we require an experimental quantity which possesses the following properties: (i) it must be sensitive to the potential used; (ii) it must be easily measured; (iii) it must be easily calculated.

We have chosen to use the atomic asymmetry parameter $\beta(E)$, which is defined in terms of the differential cross section $d\sigma(E)/d\Omega$ (see appendix B):

$$\frac{d\sigma(E)}{d\Omega} = \frac{\sigma_{tot}}{4\pi}\,[1 + \beta(E)P_2(\cos\theta)], \tag{1}$$

where σ_{tot} is the total cross section for photoionization, E is the photoelectron energy, $P_2(x) = \frac{1}{2}(3x^2-1)$, and θ is the angle of emission with respect to the polarization vector of the incident photon.[11] For an electron initially in a one-electron state $|n,\ell\rangle$, with n being the principal quantum number and ℓ being the azimuthal quantum number, the dipole selection rule restricts the final state to a superposition of continuum waves with $\ell' = \ell \pm 1$. Thus the angular distribution of photoelectrons is the result of the interference of two outgoing waves. As such, it depends upon the relative matrix

elements for transitions into these two continuum waves, and upon the phase difference of the two waves. More explicitly, $\beta(E)$ is given by the Cooper-Zare[12/] formula:

$$\beta(E) = \frac{\ell(\ell-1)R_{\ell-1}^2+(\ell+1)(\ell+2)R_{\ell+1}^2-6\ell(\ell+1)R_{\ell+1}R_{\ell-1}\cos(\delta_{\ell+1}-\delta_{\ell-1})}{(2\ell+1)[\ell R_{\ell-1}^2+(\ell+1)R_{\ell+1}^2]} \quad (2)$$

which is valid for spherically symmetric atoms in the L-S coupling scheme.

Here,

$$R_{\ell\pm1}(E) = \int_0^\infty dr\, P_{n,\ell}(r)\hat{d}P_{E,\ell\pm1}(r) \quad (3)$$

are the dipole matrix elements for the transitions $|n,\ell\rangle \longrightarrow |E,\ell\pm1\rangle$, and $\delta_{\ell\pm1}$ are the phase shifts of the continuum waves. In equation 3, $\hat{d}$ represents the dipole operator, and $P_{n,\ell}(r)/r$ $[P_{E,\ell\pm1}(r)/r]$ is the radial part of the bound [continuum] wavefunction.

The continuum functions are normalized as

$$P_{E,\ell}(r) \xrightarrow[r\to\infty]{} \left(\frac{2}{\pi k}\right)^{1/2} \sin[kr + \frac{1}{k}\ln(2kr) - \ell\frac{\pi}{2} + \delta_\ell], \quad (4)$$

where $k^2 = 2E$. This is the standard normalization per unit energy. The total cross section $\sigma_{tot}(E)$ is then given by[6/]

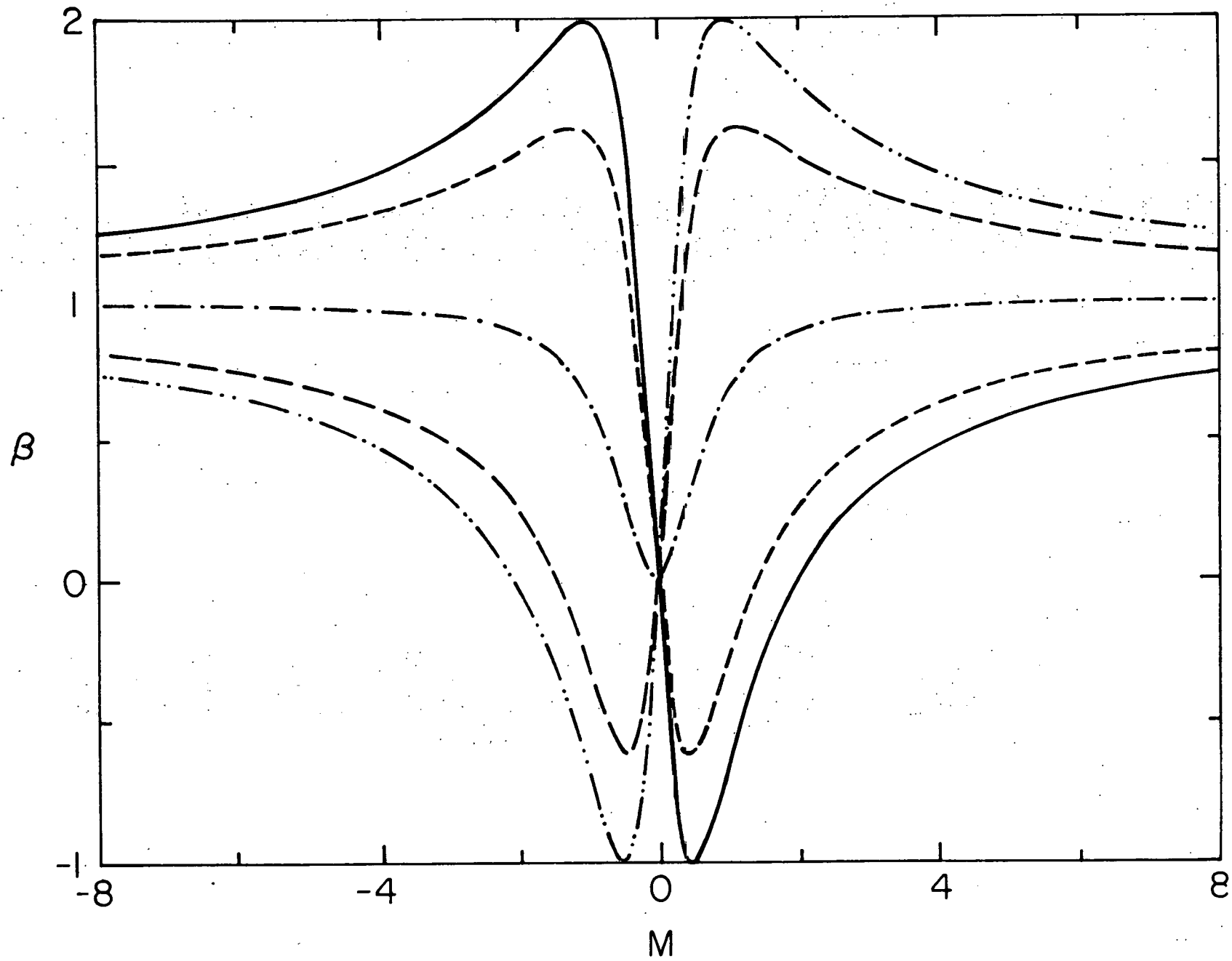
$$\sigma_{tot}(E) = \frac{4\pi^2}{3}\alpha\omega \frac{N_{n,\ell}}{(2\ell+1)}[\ell R^2_{\ell-1} + (\ell+1)R^2_{\ell+1}], \tag{5}$$

where ω is the photon energy and α is the fine structure constant.

To illustrate how β depends on the phase shifts and matrix elements, we refer the reader to Fig. 1. There, we plot β vs. $M \equiv R_{\ell+1}/R_{\ell-1}$ for several values of $\Delta \equiv \delta_{\ell+1} - \delta_{\ell-1}$, with $\ell = 1$. For the cases we will consider M lies roughly in the range $-4 < M < 4$ and Δ varies by about 2π. These ranges qualitatively explain the oscillatory behavior of $\beta(E)$ which is seen in the actual data. Note in particular the point $M = 0$ in this figure. This is the so called "Cooper minimum,"[13] and near this point β is especially sensitive to variations in both M and Δ. The dependence of β on M and Δ suggests a non-trivial dependence of $\beta(E)$ on the potential. This is verified by the calculations.

Experimentally, $\beta(E)$ can be measured with relative ease, as it requires no knowledge of absolute cross sections. Measurements are typically made with either atomic line sources or synchrontron radiation as a source of photons. Line source measurements can be made quite accurately, provided the cross section is large enough to provide adequate counting rates. In effect, this limits such measurements to electron energies below the Cooper minimum. One is further limited in energy selection by the discrete spectra of these sources. These

Fig. 1. Asymmetry parameter β as a function of $M = R_2/R_0$;
—— ($\Delta = 0$); --- ($\Delta = \pi/4$); —— · —— ($\Delta = \pi/2$);
—— —— ($\Delta = 3\pi/4$); —— ·· —— ($\Delta = \pi$).


2
1
0
-1
β
-8
-4
0
4
8
M

problems are alleviated by the use of synchrotron radiation, which provides a strong continuum of radiation in the far UV to x-ray region. The trade off here is that it is difficult to maintain a constant polarization with these sources.[14]

In calculating $\beta(E)$ we take the bound state wavefunction, $P_{n,\ell}$, from HF calculations of the ground state[15-16], since these are generally considered to be accurate. For the continuum waves we assume the Schrödinger equation:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{(\ell\pm1)(\ell\pm1+1)}{2r^2} + V(r) - E\right]P_{E,\ell\pm1}(r) = 0, \quad (6)$$

with $V(r)$ the pseudopotential which is to be determined. This equation is solved numerically for a given potential by Numerov[17] integration. Since at large distances from the nucleus the electron sees the residual ion as a point charge of +1, we normalize $P_{E,\ell}(r)$ by matching the numerical solutions of equation (6) to Coulomb functions at large r:

$$P_{E,\ell}(r) = (a_\ell(E)F_\ell(-\frac{1}{k},kr) + b_\ell(E)G_\ell(-\frac{1}{k},kr), \quad (7)$$

where $k^2 = 2E$ and $F_\ell(G_\ell)$ is the regular (irregular) Coulomb function. We obtain the phase shift at the same time from the relation

$$\delta_\ell(E) = \sigma_\ell(E) - \tan^{-1}[a_\ell(E)/b_\ell(E)], \quad (8)$$

where $\sigma_\ell = \mathrm{Arg}\Gamma(\ell+1-ik)$ is the Coulomb phase shift.

Dipole matrix elements are obtained by Simpson's rule integration of equation (3) with $\hat{d}$ defined as

$$\hat{d} \equiv \frac{1}{2}(\hat{d}_L + \hat{d}_V), \tag{9}$$

where $\hat{d}_L = r$ is the length form of the dipole operator and

$$\hat{d}_V = \frac{-1}{\omega}\left[\frac{d}{dr} + (1-2\delta_{\ell',\ell+1})\frac{1+\delta_{\ell',\ell+1}}{r}\right] \tag{10}$$

is the velocity form of the dipole operator. (Here δ is a Kronecker delta.)

In choosing this form of the dipole operator, we have been guided by consideration of the f-sum rule (see ref. 6 and Appendix A)

$$N = \sum_{n,\ell}\left[\sum_{n',\ell'} f_{n\ell\to n'\ell'} + \frac{1}{2\pi^2\alpha}\int_{I_{n\ell}}^{\infty}\sigma_{n\ell}(\omega)\,d\omega\right], \tag{11}$$

where N is the total number of electrons in the atom, $f_{n\ell\to n'\ell'}$ is the oscillator strength for transitions to the bound state $|n',\ell'\rangle$, and $I_{n\ell}$ is the ionization potential of the state $|n,\ell\rangle$. The first sum is over all initial electron orbitals and the second is over all bound excited orbitals.

In all completely local theories, as well as in the RPAE, the length and velocity operators are equivalent. This is also the case for exact wavefunctions, as it is essentially a statement of $\hat{v} \equiv i[H,\hat{r}] = \hat{p}$, where $\hat{v}$ and $\hat{p}$ are the

electron velocity and momentum operators, respectively. In the HF case, however, $\hat{v}$ is not proportional to $\hat{p}$, the two dipole operators are not equivalent, and the choice of either $\hat{d}_L$ or $\hat{d}_V$ fails to satisfy the f-sum rule. Amusia has shown[6/] that this situation may be remedied in large part by our choice of $\hat{d}$. For the pseudopotential calculations the HF situation holds, due to the use of HF bound states. Thus our choice of dipole operator seems reasonable.

We have described above, the calculation of $\beta(E)$ for a given potential, $V(r)$. In order to determine $V(r)$ uniquely we have chosen $V(r)$ to be of the form $V(r) = -Z(r)/r$ with

$$Z(r) = 1 + (Z_0-1)\frac{(1-r/C)^2}{(1+Ar+Br^2)}\,\theta(C-r). \tag{12}$$

Z_0 is the nuclear charge, $\theta(x < 0) = 0$, $\theta(x \geq 0) = 1$, and A,B,C are adjustable parameters. This form of the effective charge, $Z(r)$, has the correct asymptotic values at both large and small values of r. The form in the intermediate region is reminiscent of the Pade approximant[18/] which has proved to be a useful method of approximation. Note also, that $Z(C) = 1$ and $Z'(C) = 0$, so that C should correspond roughly to the radius of the ion.

Values of the parameters A,B, and C are obtained by minimization of the function

$$f(A,B,C) = \sum_i [\beta^{exp}(E_i)-\beta^{calc}(E_i,A,B,C)]^2 w_i \tag{13}$$

where β^{exp} and β^{calc} are the experimental and calculated values, respectively, w_i is a weight factor, and the E_i are the selected set of energies at which β has been measured.

To illustrate the sensitivity of $\beta(E)$ to $V(r)$ we consider photoionization of the 3p subshell of Ar. In Fig. 2 we plot two curves of $Z(r)$ which are nearly coincident. In Fig. 3 we plot the corresponding results for $\beta(E)$ and note that the two results differ significantly one from the other.

Fig. 2. Representative effective charges for photoionization of the Ar 3p level.

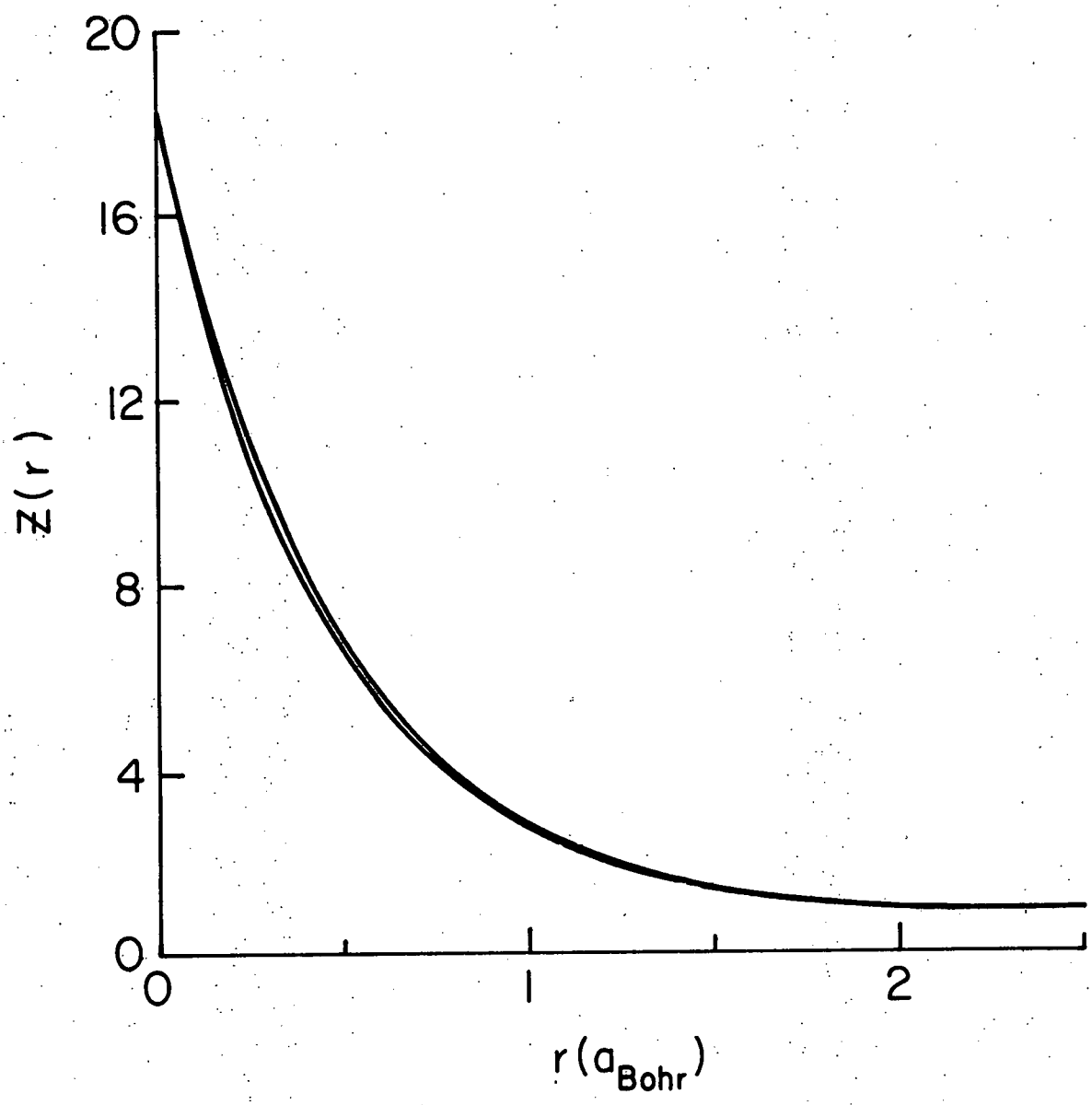
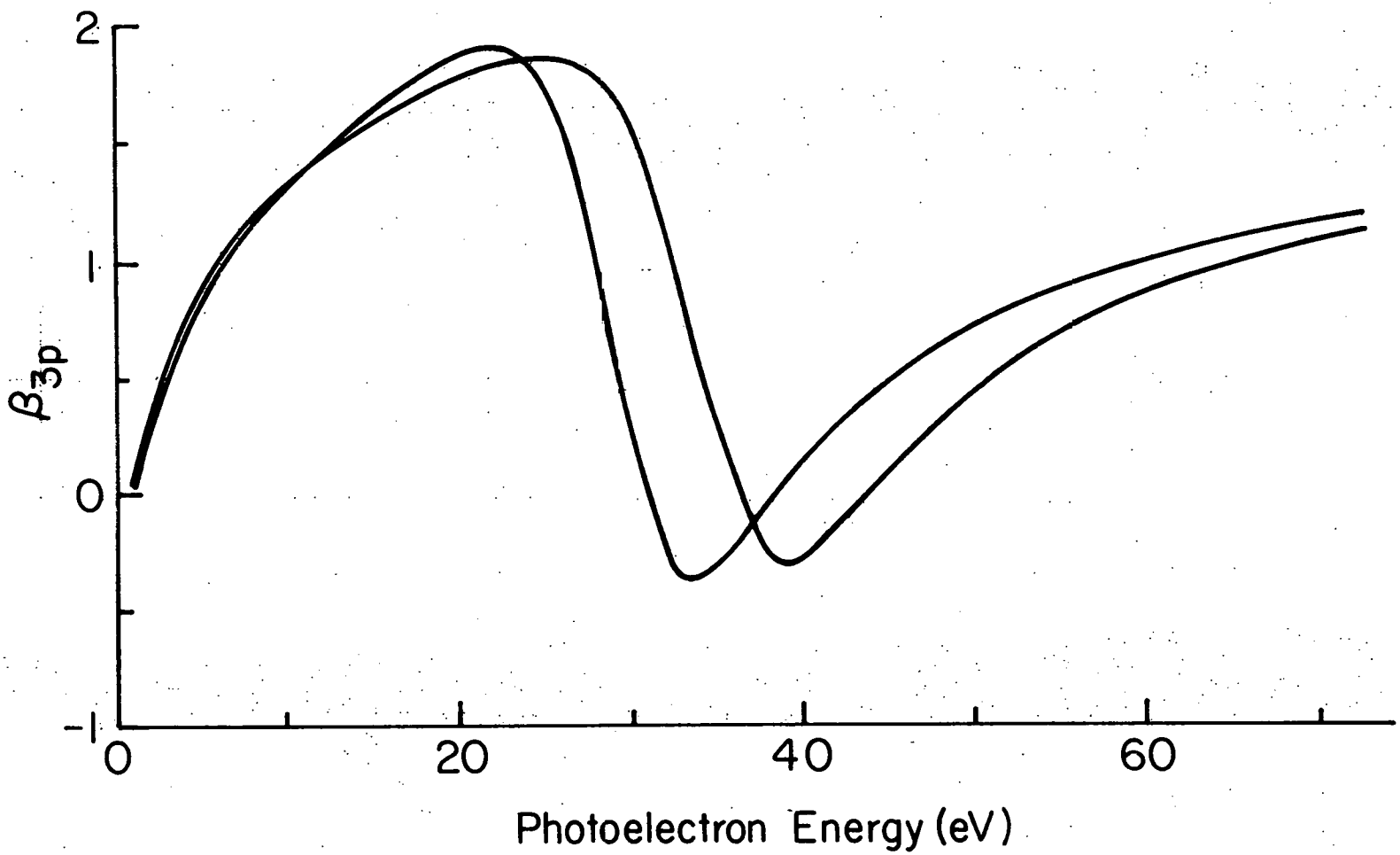

20
16
12
8
4
0
Z(r)
0
1
2
r (a_Bohr)

Fig. 3. Asymmetry parameters obtained from the effective charges shown in Fig. 2.


2
1
0
-1
β_{3p}
0
20
40
60
Photoelectron Energy (eV)

IV. RESULTS

A. Argon

In analyzing photoionization of the Ar 3p subshell, we have used measured values[19] of $\beta(E)$ at energies of 5.4, 11, and 25 electron volts (eV), with a weight factor $w_i = 1$ for each energy. Optimum values of the parameters A,B,C for each case are given in Table I.

In Figure 4 we compare the experimental measurements of $\beta(E)$ to calculations performed by HF-length[5] (HF-L), HF-Velocity[5] (HF-V), RPAE,[6] and pseudopotential methods. We see that each of the theories exhibits the general structure, but only the RPAE and pseudopotential calculations are quantitatively correct. It should be pointed out that the data used in the pseudopotential analysis are all well below the Cooper minimum and suggest very little of the overall structure of $\beta(E)$. In addition, the data above 35 eV[14] were obtained subsequent to this analysis and serve to confirm the accuracy of the pseudopotential for a large range of electron energies.

In Figure 5 we compare HKS,[1] X_α [1] and pseudopotential calculations of $\beta_{3p}(E)$. This figure demonstrates, in part, the inadequacy of the standard local density theories. More detailed discussion of local density theories may be found in reference 1.

Figure 6 compares calculated and experimental cross sections for Ar 3p photoionization. Again, only the pseudopotential and RPAE calculations may be considered quantitatively correct.

Table I. Effective Charge Parameters

Initial State	A	B	C
Ar 3p	1.122	.739	2.248
Kr 4p	2.852	-.230	2.144
Xe 5p	2.957	1.096	2.758
X3 4d	3.853	3.024	5.099

Fig. 4. Asymmetry parameter, $\beta(E)$, for the 3p subshell of Ar: —— (present work); ---- (RPAE, Ref. 6); ——·—— (HF-Length, Ref. 5); ——··—— (HF-Velocity, Ref. 5); o (Houlgate *et al.*, Ref. 14); · (Dehmer *et. al.*, Ref. 19); ■ (Watson and Stewart, Ref. 20). Arrows indicate data used to determine V(r).

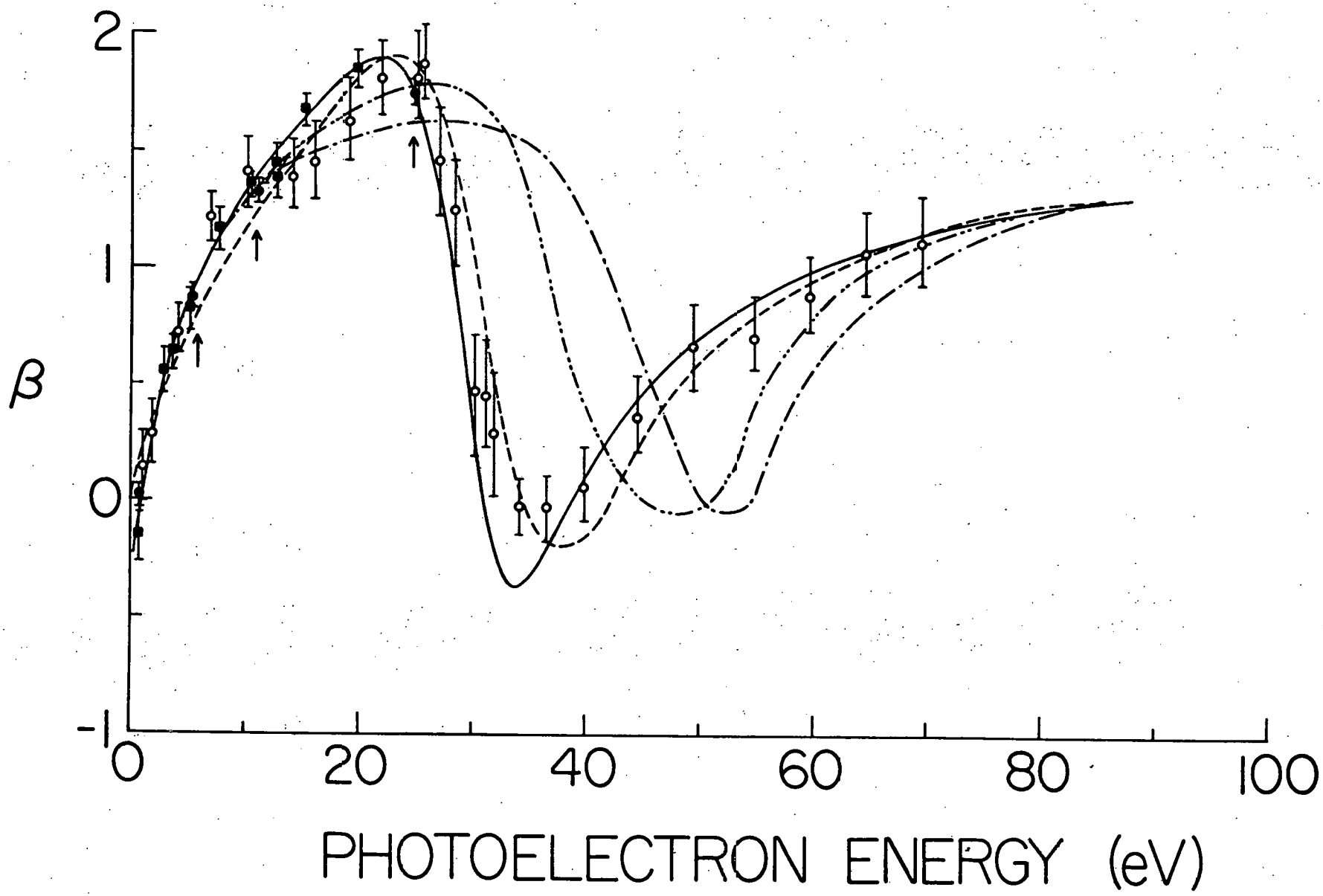

2
1
0
-1
β
0
20
40
60
80
100
PHOTOELECTRON ENERGY (eV)

Fig. 5. Comparison of HKS (····), X_α (---), and pseudopotential (——) calculations of $\beta(E)$ for photoionization of the 3p level of Ar.

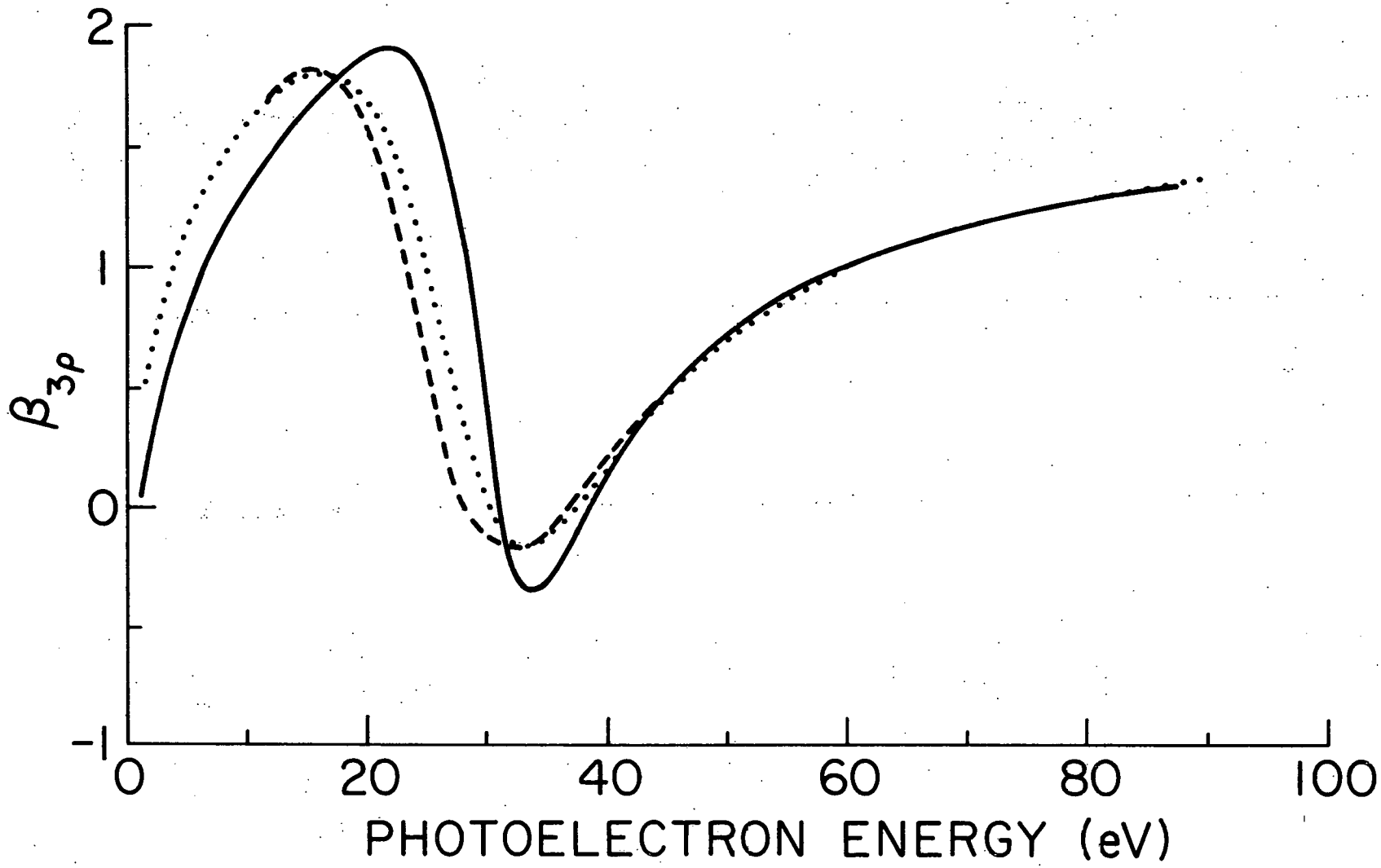
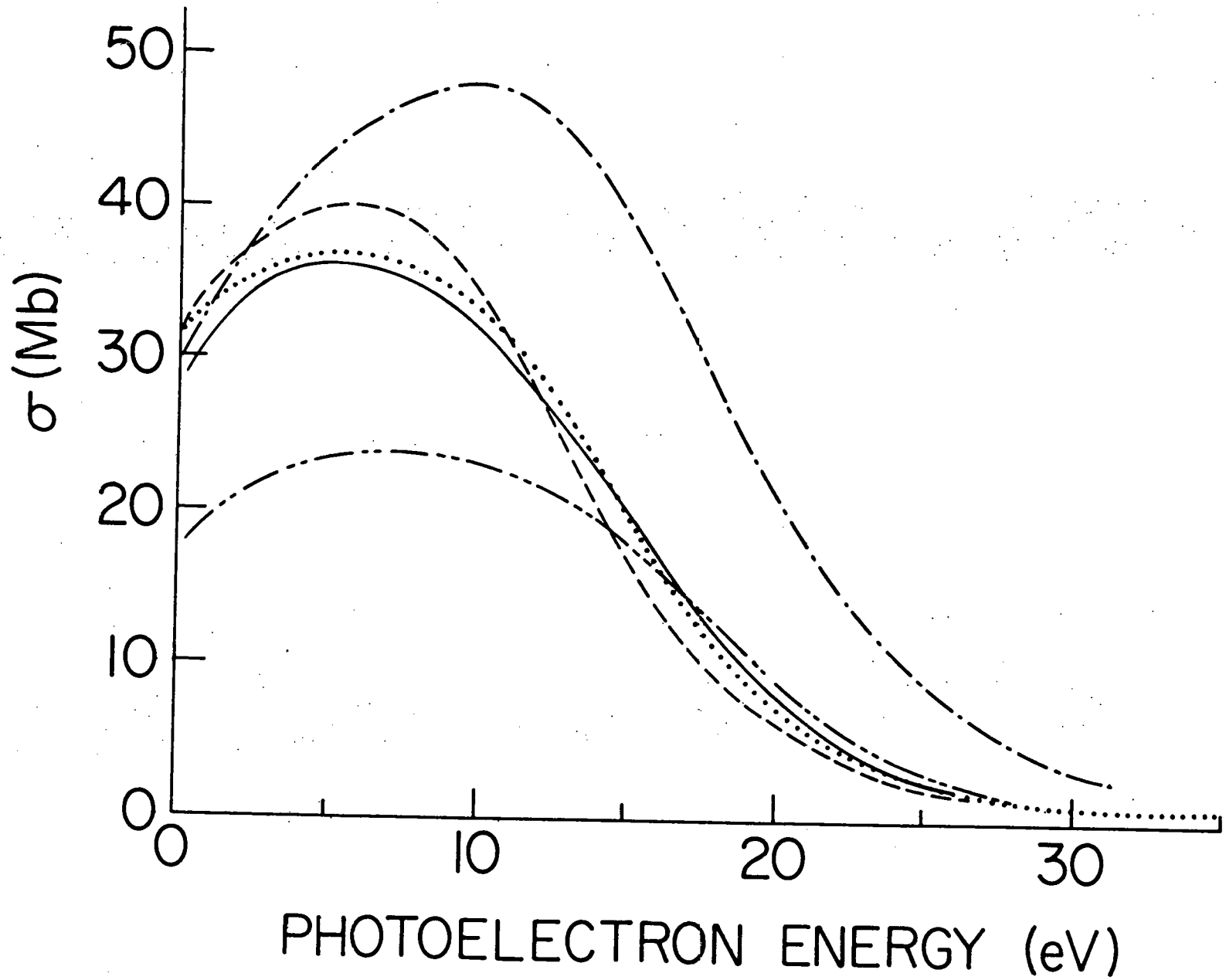

2
1
0
-1
β_{3p}
0
20
40
60
80
100
PHOTOELECTRON ENERGY (eV)

Fig. 6. Photoionization cross section for the 3p subshell of Ar: .... (Experiment, Ref. 21); —— (present work); ---- (RPAE, Ref. 6); ——·—— (HF-L, Ref. 5); ——··—— (HF-V, Ref. 5).


σ (Mb)
50
40
30
20
10
0
0
10
20
30
PHOTOELECTRON ENERGY (eV)

To aid the reader in visualizing the potential we have obtained, we show in Figure 7 the pseudopotential effective charge, $Z(r)$, as well as the effective charge, $Z_{H,3p}$, of a Hartree potential obtained from the ground state Ar wavefunction:

$$Z_{H,n\ell} = r \sum_{n',\ell'} (2\ell'+1)V_{n',\ell'}(r) - rV_{n\ell} \tag{14}$$

where

$$V_{n,\ell}(r) = \int_r^\infty dr' P^2_{n,\ell}(r')/r' + \frac{1}{r}\int_0^r P^2_{n\ell}(r')dr'. \tag{15}$$

We note that the pseudopotential is stronger near the nucleus than is the Hartree potential, and that the principal effect of this is to shift the Cooper minimum to a lower energy.

Our first attempt to describe photoionization of s states was to use the Ar 3p pseudopotential for the Ar 3s level. The cross sections obtained in this way were much too high. We then fit to the 3p cross section (since $\beta_{3s} = 2$, angular distributions yield no information), obtaining

$$Z_{3s}(r) = 1 + (Z_0-1)[e^{-r/R} - .35(r/R)e^{-1.6r/R} - .58(r/R)(1-.84/R)e^{-1.6r/R}], \tag{16}$$

with $R = .49$. The results of this fit are displayed in Figure 8. In Figure 9 we compare Z_{3s} with $Z_{H,3s}$ and note that the 3s potential is much closer to the Hartree potential than is the 3p potential (Figure 7).

Fig. 7. Comparison of pseudopotential effective charge (——) and Hartree effective charge (----) for photoionization of the 3p level of Ar.

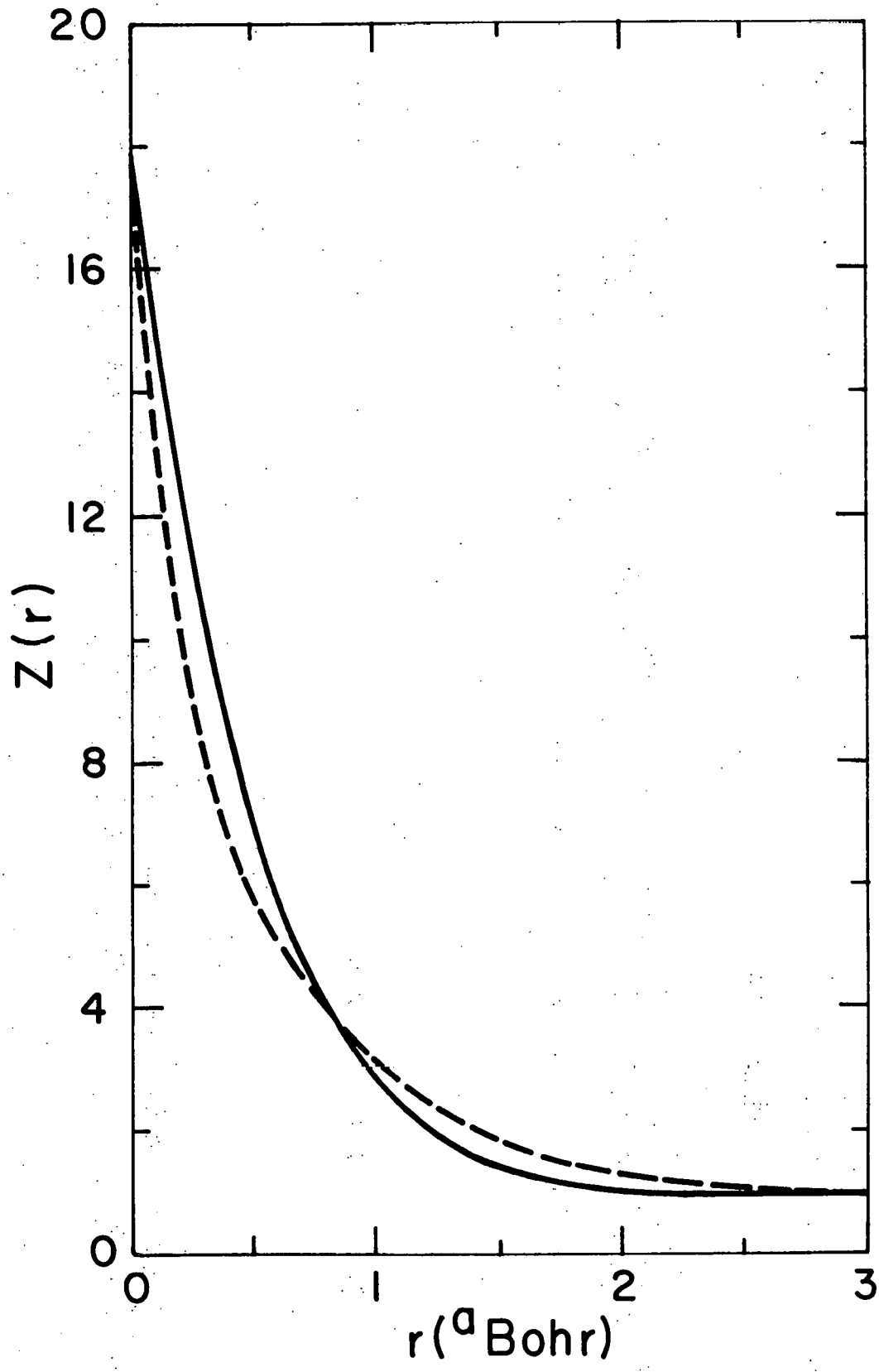

20
16
12
8
4
0
Z(r)
0
1
2
3
r(aBohr)

Fig. 8. Ar 3s photoionization cross sections: —— (present work); ---- (RPAE, Ref. 6); ——·——· (HF-L, Ref. 5); ···· (R-Matrix, Ref. 22); x (Samson and Gardner, Ref. 23); o (Torop *et al.*, Ref. 24).

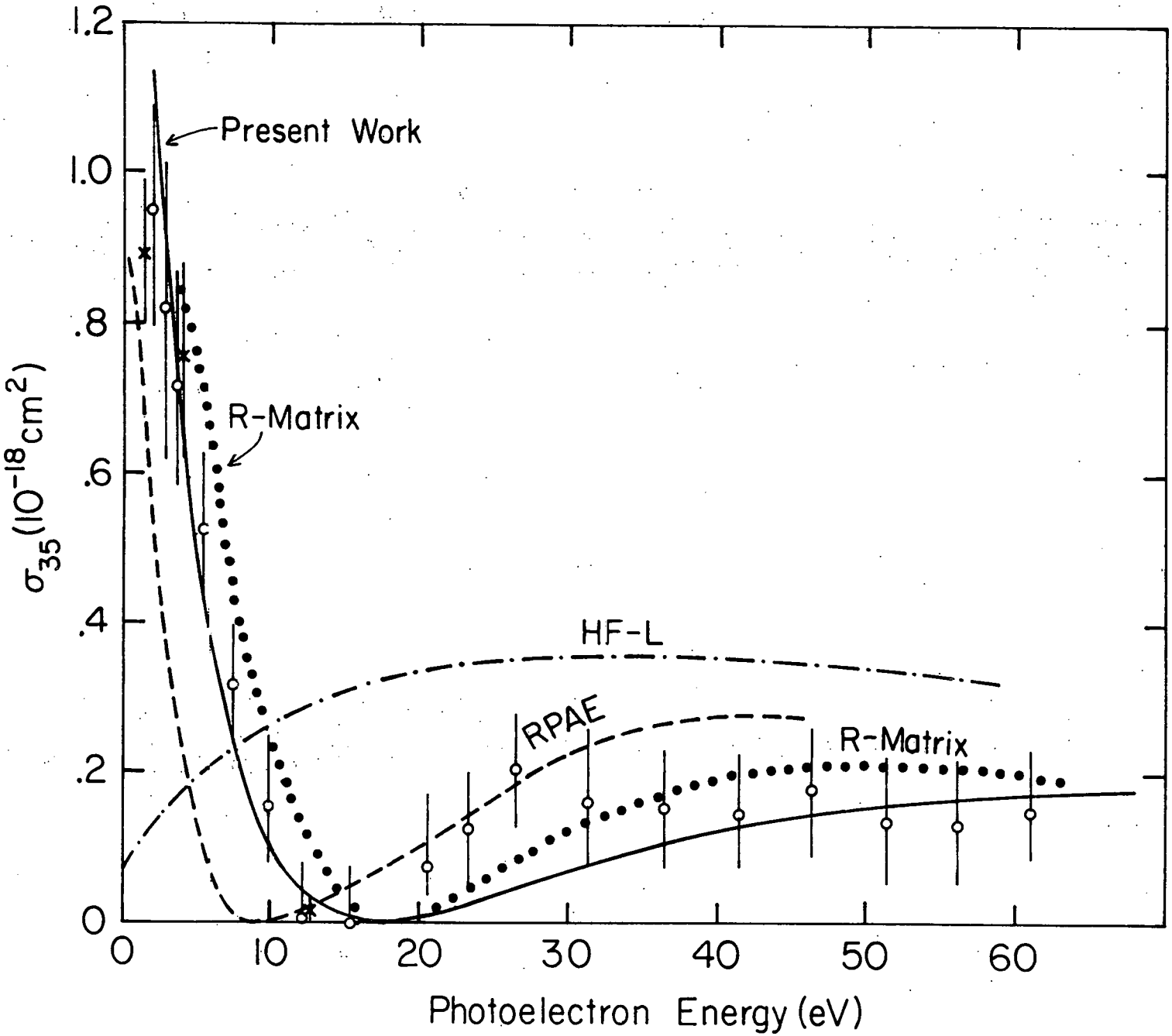
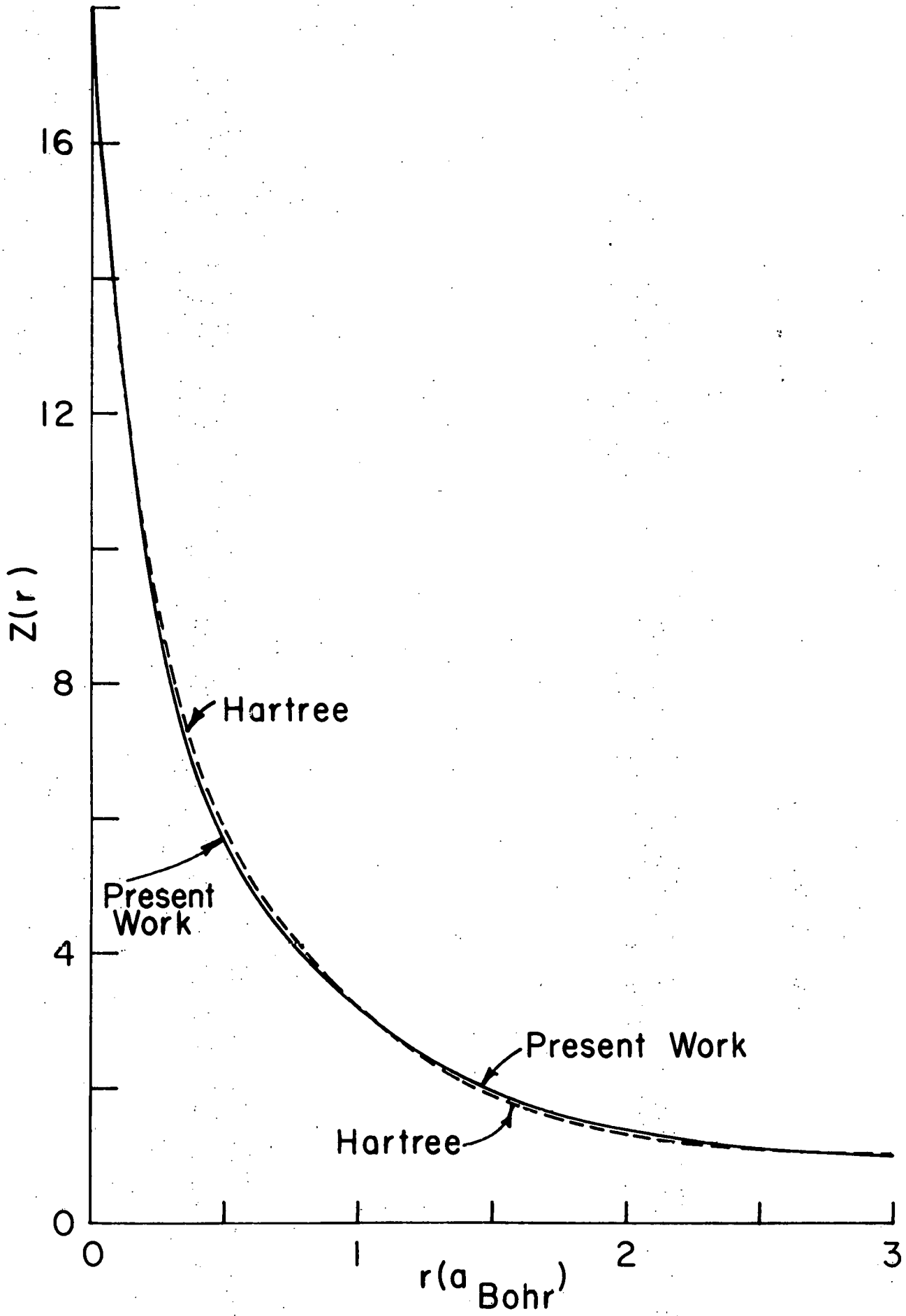

1.2
1.0
.8
.6
.4
.2
0
$\sigma_{35}(10^{-18}cm^2)$
Present Work
R-Matrix
HF-L
RPAE
R-Matrix
0
10
20
30
40
50
60
Photoelectron Energy (eV)

Fig. 9. Comparison of pseudopotential (——) and Hartree (----) effective charges for photoionization of the 3s level of Ar.


16
12
8
4
0
Z(r)
Hartree
Present
Work
Present Work
Hartree
0
1
2
3
r(a Bohr)

B. Krypton and Xenon

We consider next photoionization from the Kr 4p, Xe 5p, and Xe 4d subshells. For these analyses the weight factor w_i was taken to be the inverse square of the standard deviation σ: $w_i = \sigma_i^{-2}$. For Kr 4p we have used experimental measurements taken at the NINA synchrotron[23]. For Xe 5p and 4d we have used data from references 19 and 24. The results for $\beta(E)$ are displayed in Figures 10-12, and the cross sections are shown in Figures 13-15. The basic conclusions of the Ar 3p analysis are also true here: only RPAE and pseudopotential are quantitative, and proper location of the Cooper minimum is important in the description of $\beta(E)$. An exception is the Xe 4d case, where the pseudopotential cross section is larger than the experimental values. We attribute this discrepancy to the lack of suitable angular distribution data. The present data fail to define the energy of the Cooper minimum. No attempt was made here to incorporate the cross sections into the analysis.

The abrupt increase of β_{5p}^{exp} above the Cooper minimum will be discussed further in Section IV.D.

C. Continuum Phase Shifts, Quantum Defects, and Dipole Matrix Elements

In Figures 16-17 we compare continuum pseudopotential phase shifts to those of HF[5] and Hartree-Slater (HS)[27] calculations. Integral multiples of 2π were added to the current results where necessary, to bring them into near coincidence

Fig. 10. Asymmetry parameter, $\beta(E)$, for the 4p subshell of Kr: —— (present work); ---- (RPAE, Ref. 6); ——· —— (HF-L, Ref. 5); —— ·· —— ·· (HF-V, Ref. 5); o (Miller *et al.*, Ref. 25); ■ (Dehmer *et al*, Ref. 19).

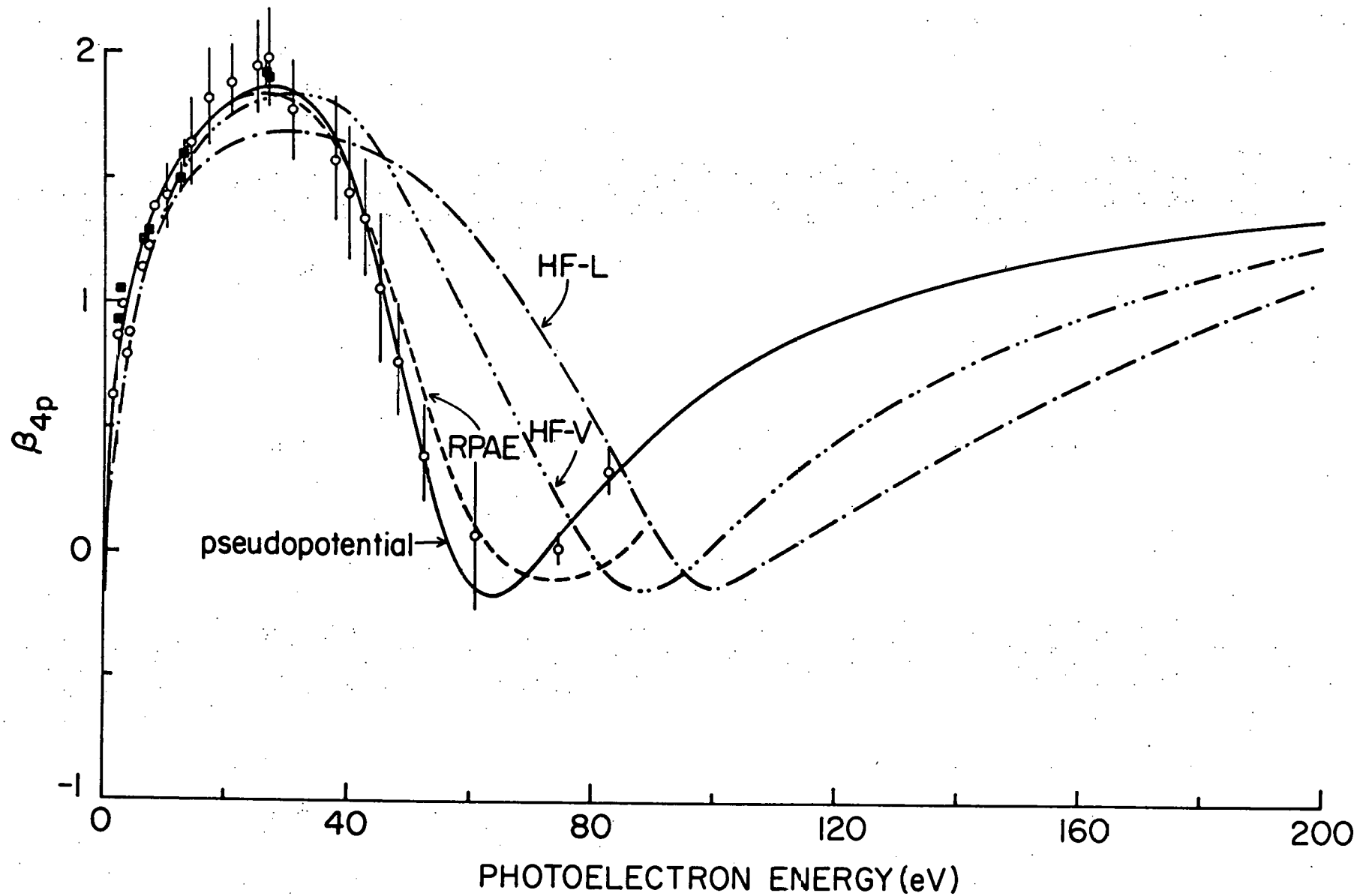

2
1
0
-1
β_{4p}
0
40
80
120
160
200
PHOTOELECTRON ENERGY (eV)
HF-L
HF-V
RPAE
pseudopotential

Fig. 11. Asymmetry parameter, $\beta(E)$, for the 5p subshell of Xe: —— (present work); ---- (RPAE, Ref. 6); —— ·· —— (HF-L, Ref. 5); ——·——· (HF-V, Ref. 5); —— —— —— (HS, Ref. 5); · (Torop *et al.*, Ref. 24); ■ (Dehner *et al.*, Ref. 19).

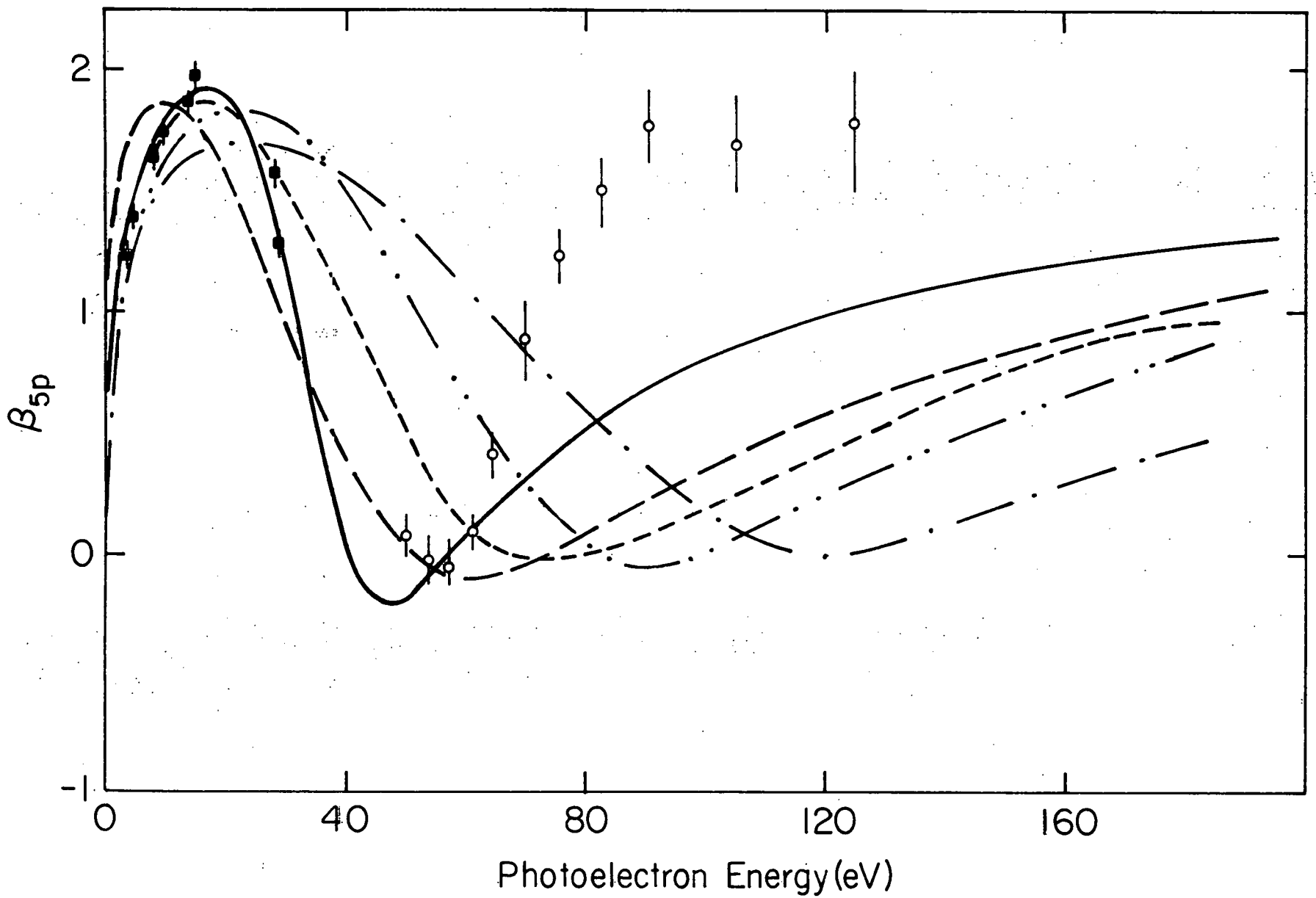

2
1
0
-1
β_{5p}
0
40
80
120
160
Photoelectron Energy (eV)

Fig. 12. Asymmetry parameter, $\beta(E)$, for the 4d subshell of Xe: —— (present work); ---- (RPAE, Ref. 7); ——·——· (HF-L, Ref. 5); —— ·· ——·· (HF-V, Ref. 5); o (experiment, Ref. 24).

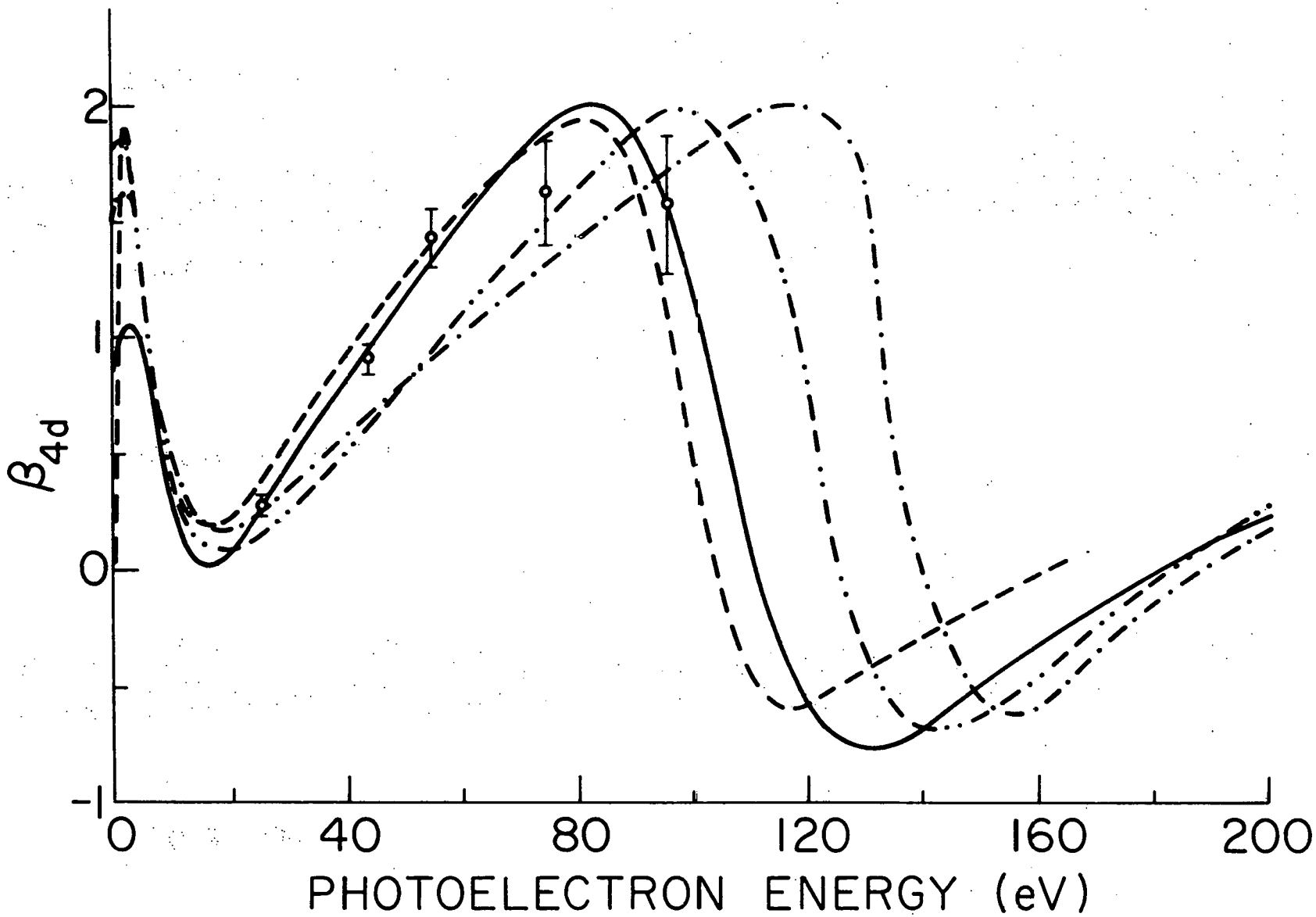

β_{4d}
2
1
0
-1
0
40
80
120
160
200
PHOTOELECTRON ENERGY (eV)

Fig. 13. Photoionization cross section for the 4p subshell of Kr: —— (present work); ---- (RPAE, Ref. 6); ——·—— (HF-L, Ref. 5); ——··——·· (HF-V, Ref. 5); .... (experiment, Ref. 26).

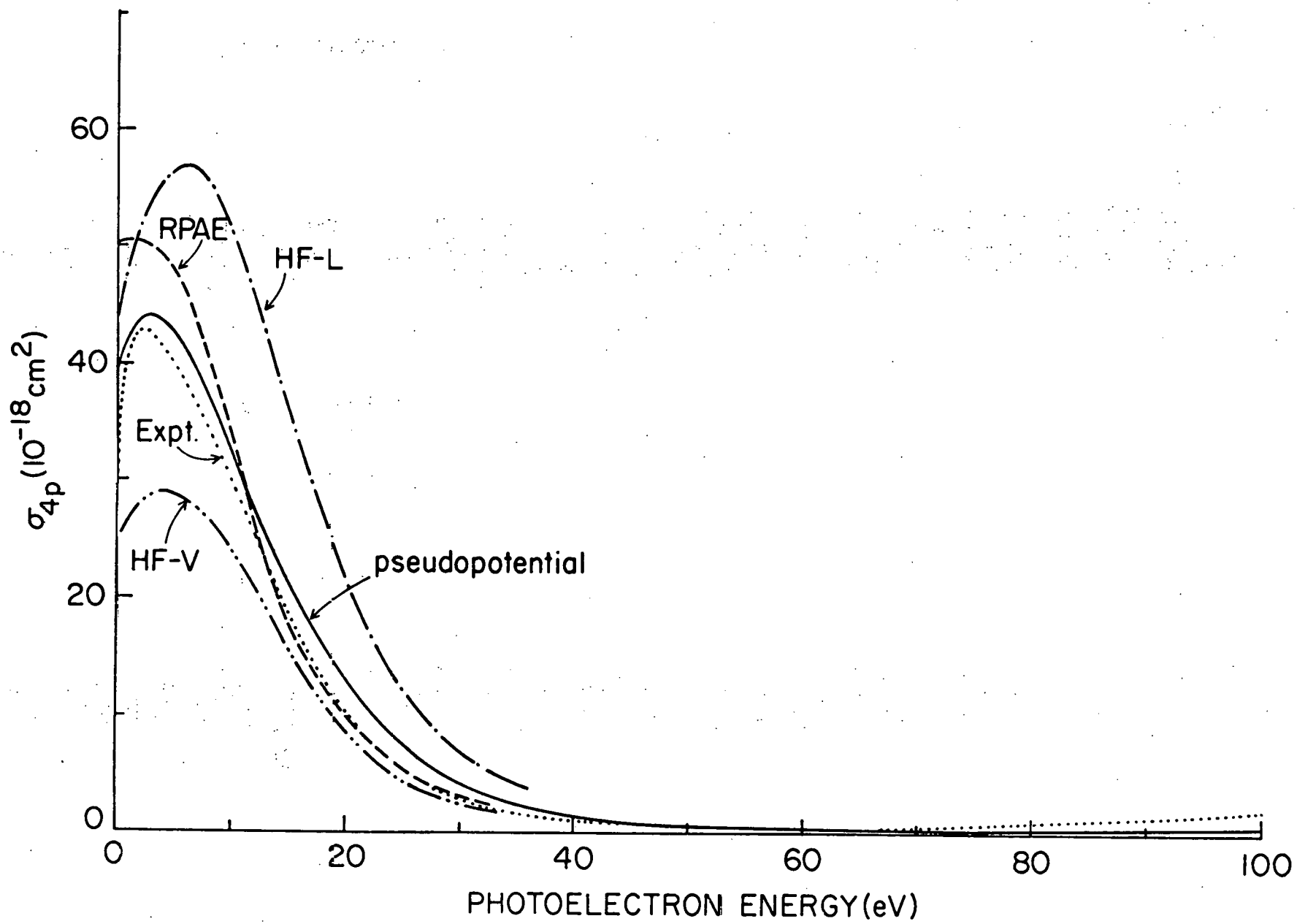

60
40
20
0
$\sigma_{4p}(10^{-18}cm^2)$
RPAE
HF-L
Expt.
HF-V
pseudopotential
0
20
40
60
80
100
PHOTOELECTRON ENERGY(eV)

Fig. 14. Photoionization cross section for the 5p subshell of Xe: —— (present work); ---- (RPAE, Ref. 6); ——·——· (HF-L, Ref. 5); ——··——·· (HF-V, Ref. 5); ···· (experiment, Ref. 21).

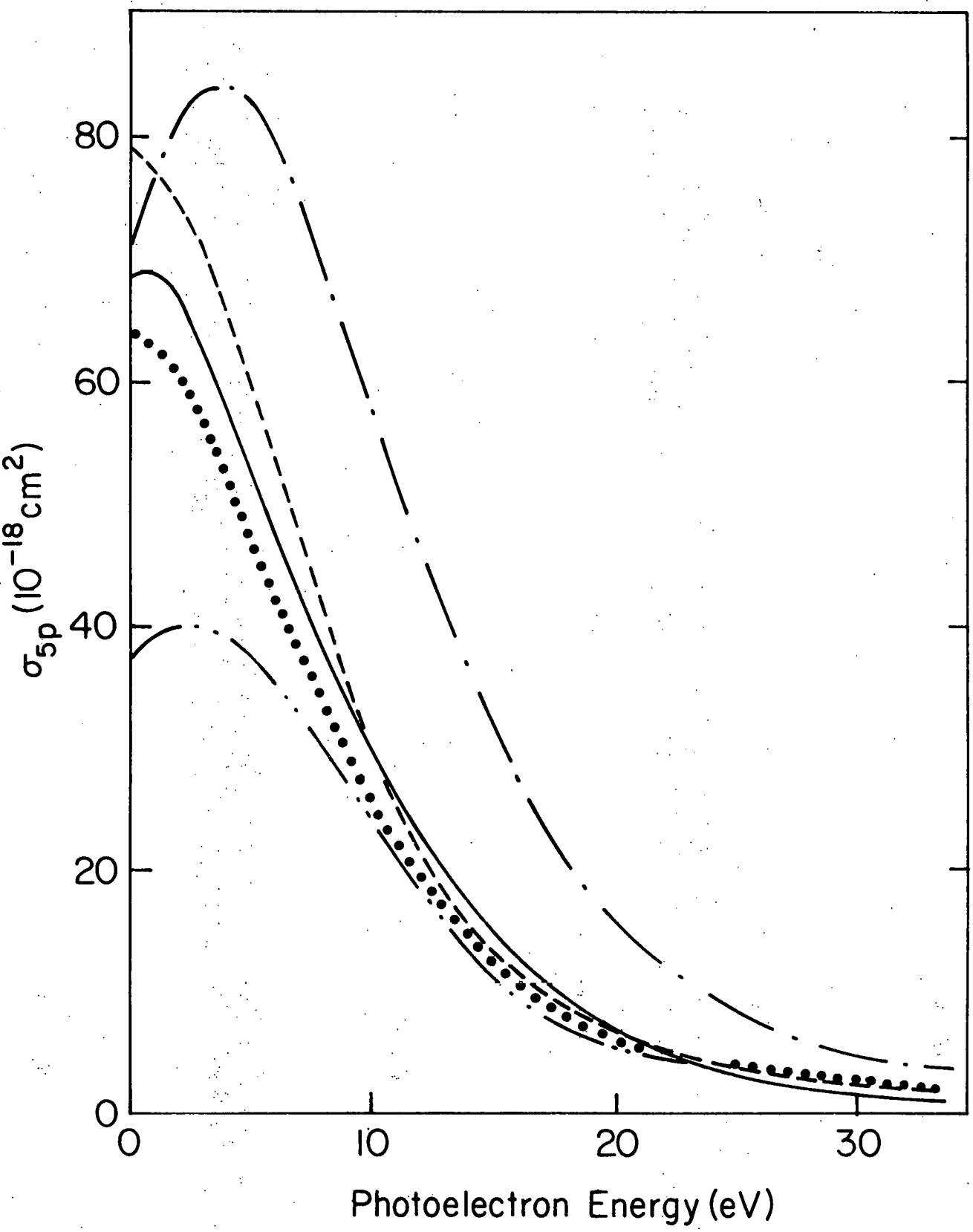

80
60
40
20
0
σ_{5p} (10^{-18} cm^2)
0
10
20
30
Photoelectron Energy (eV)

Fig. 15. Photoionization cross section for the 4d subshell of Xe: —— (present work); ---- (RPAE, Ref. 9); ——··——·· (HF-L, Ref. 5); ——·——· (HF-V, Ref. 5); o (experiment, Ref. 28).

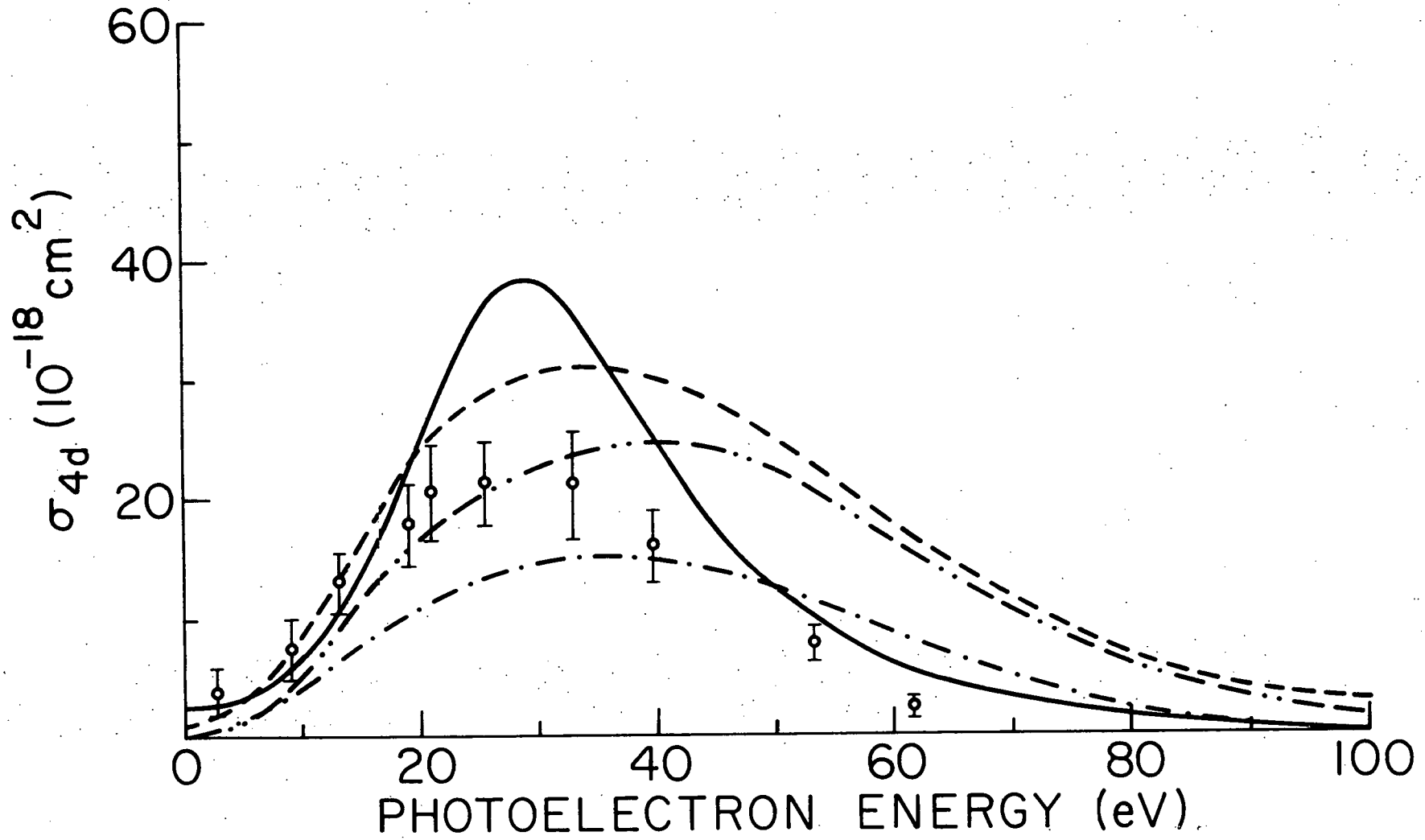

60
40
20
0
20
40
60
80
100
σ_{4d} (10^{-18} cm^2)
PHOTOELECTRON ENERGY (eV)

Fig. 16. s-wave phase shifts for photoionization of Ar 3p, Kr 4p, and Xe 5p subshells: —— (present work); ——·——· (HF, Ref. 5); —— —— —— (HS, Ref. 27).

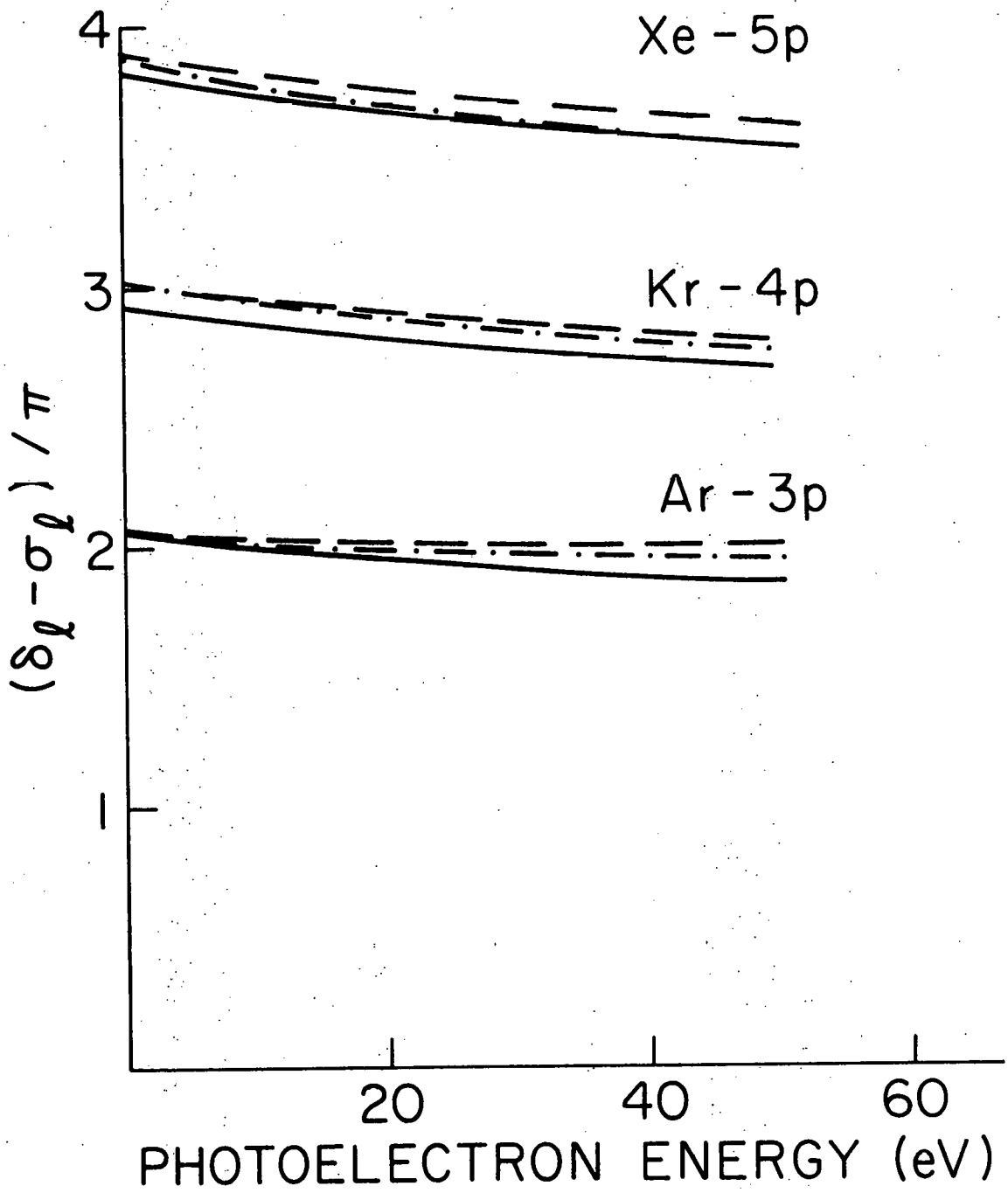
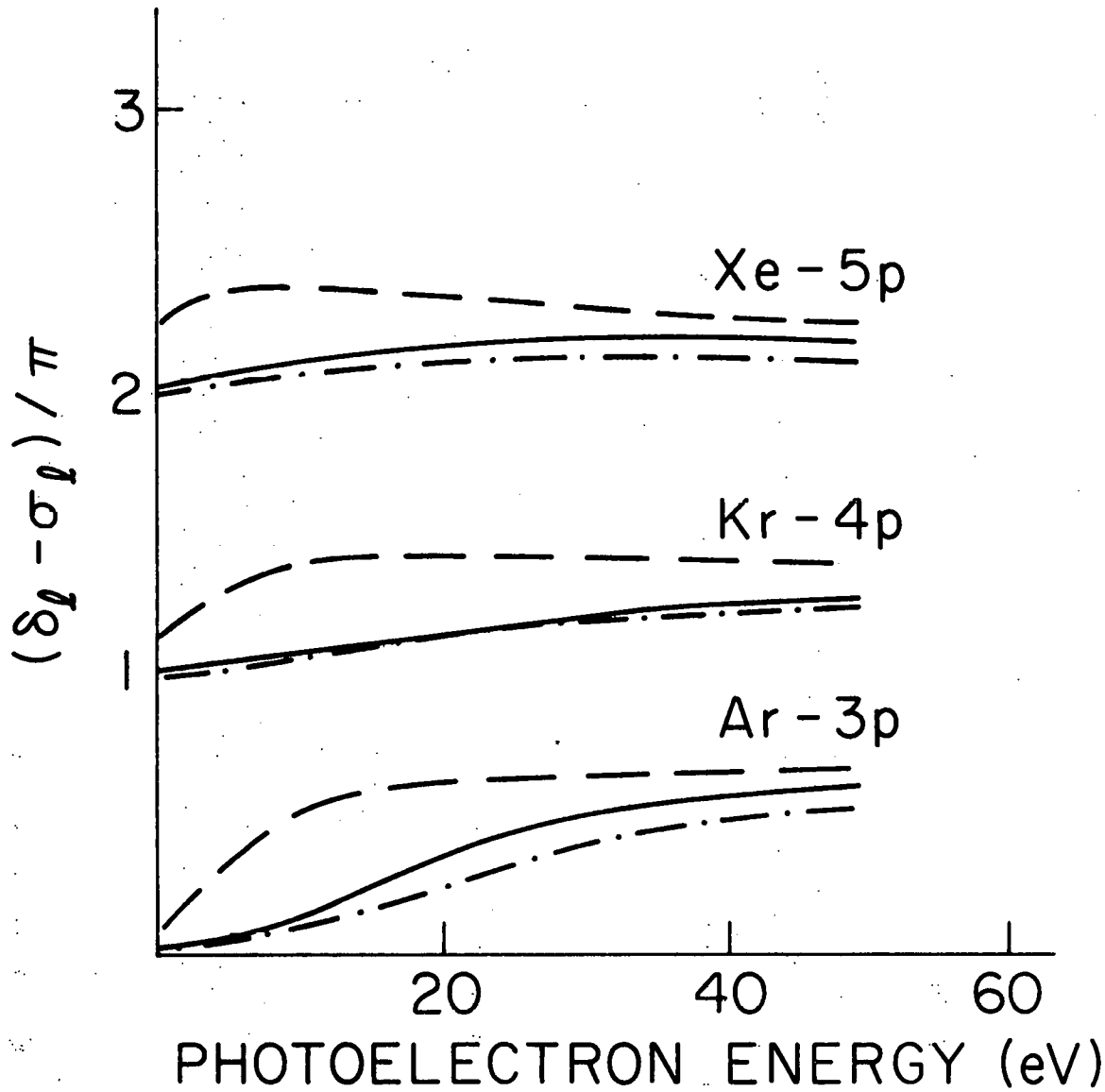

Xe - 5p
Kr - 4p
Ar - 3p
4
3
2
1
$(\delta_\ell - \sigma_\ell)/\pi$
20
40
60
PHOTOELECTRON ENERGY (eV)

Fig. 17. d-wave phase shifts for photoionization of Ar 3p, Kr 4p, and Xe 5p subshells: —— (present work); ——·——· (HF, Ref. 5); —— —— —— (HS, Ref. 27).


3
2
1
$(\delta_\ell - \sigma_\ell)/\pi$
Xe - 5p
Kr - 4p
Ar - 3p
20
40
60
PHOTOELECTRON ENERGY (eV)

with the HF results. We note that the pseudopotential and HF phases are in good agreement throughout, while the HS d-wave phase shifts differ from either of these. This difference contributes significantly to the failure of local density theories to describe $\beta(E)$.

An additional connection to experimental results is provided by the zero energy phase shifts. Seaton[29] has shown that these are related to the $n = \infty$ quantum defect, D_ℓ, by:

$$D_\ell = [\delta_\ell(0)-\sigma_\ell(0)]/\pi \tag{17}$$

where $\sigma_\ell(E)$ is the Coulomb phase shift of equation (8), and D_ℓ is defined by

$$\lim_{n\to\infty} E_{n,\ell} = -\frac{13.6\text{eV}}{(n+D_\ell)^2} . \tag{18}$$

Table II lists HF, HS, pseudopotential, and experimental[30] values of D_0 and D_2.

For the sake of completeness, we plot in figures 18-21 the continuum dipole matrix elements from the pseudopotential calculations.

D. Intershell Effects in Xenon

We now turn our attention to the anomaly in the Xe 5p asymmetry parameter. We should point out, first of all, that the onset of this anomaly occurs roughly at the threshold for

Table II. Experimental and theoretical quantum defects

Final state hole	Ar 3p		Kr 4p		Xe 5p		Xe 4d	
	D_0	D_2	D_0	D_2	D_0	D_2	D_1	D_3
Hartree-Fock[5]	2.06	0.01	3.03	1.00	3.88	2.00	3.48	0.00
Hartree-Slater[27]	2.09	0.10	3.03	1.11	3.91	2.22	3.48	0.00
Pseudopotential	2.06	0.01	2.91	1.01	3.82	2.01	3.34	0.01
Experiment[30]	2.15 ±.02	0.15 ±.02	3.09 ±.02	1.23 ±.07	4.02 ±.001	2.44 ±.006	3.54 ±.004	0.04 ±.01

Fig. 18. s- and d-wave dipole matrix elements for photoionization of the Ar 3p subshell.

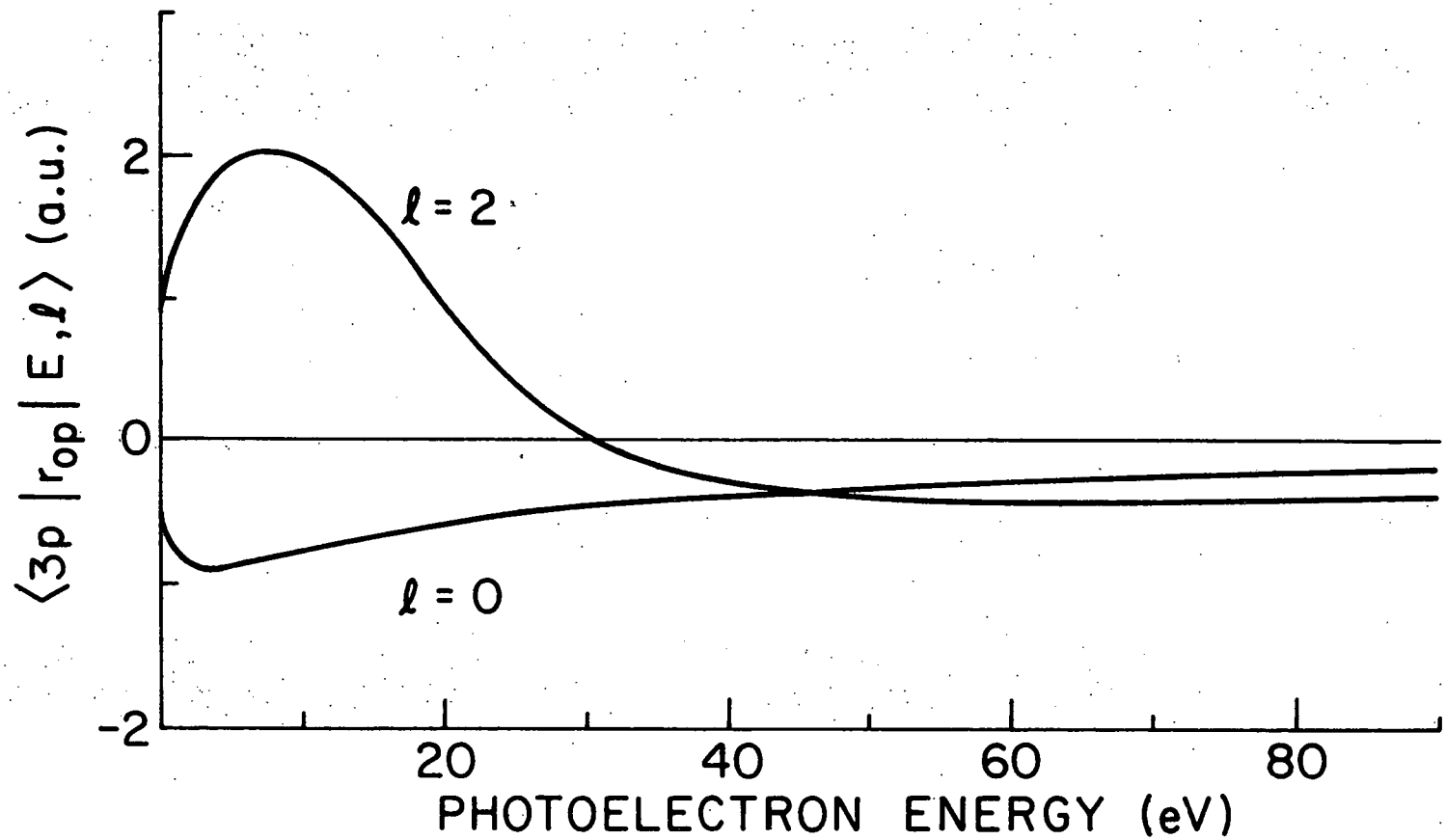

$\langle 3p | r_{op} | E, \ell \rangle$ (a.u.)
2
0
-2
$\ell = 2$
$\ell = 0$
20
40
60
80
PHOTOELECTRON ENERGY (eV)

Fig. 19. s- and d-wave dipole matrix elements for photoionization of the Kr 4p subshell.

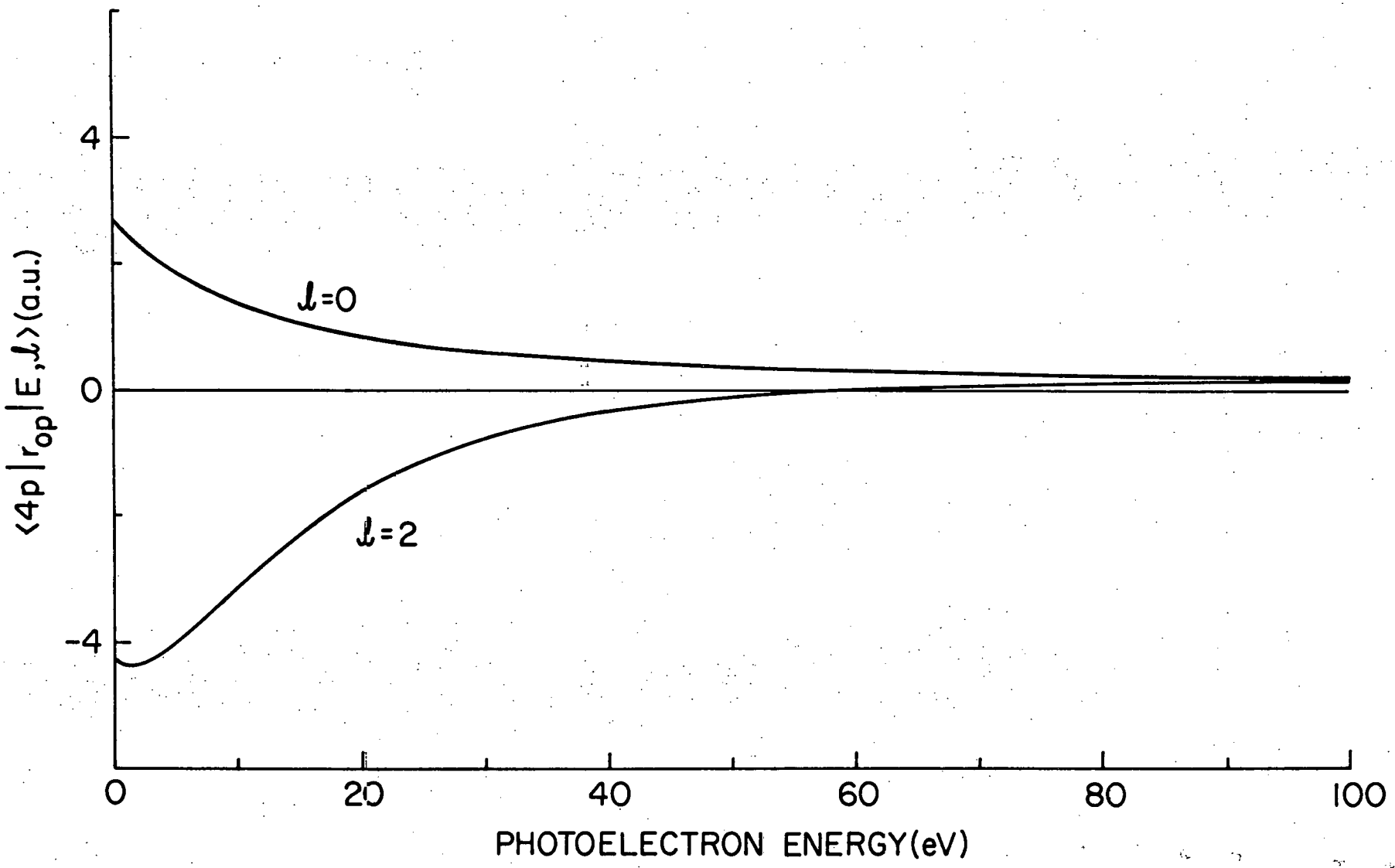

4
0
-4
$\langle 4p | r_{op} | E, \ell \rangle$ (a.u.)
$\ell = 0$
$\ell = 2$
0
20
40
60
80
100
PHOTOELECTRON ENERGY(eV)

Fig. 20. s- and d-wave dipole matrix elements for photoionization of the Xe 5p subshell.

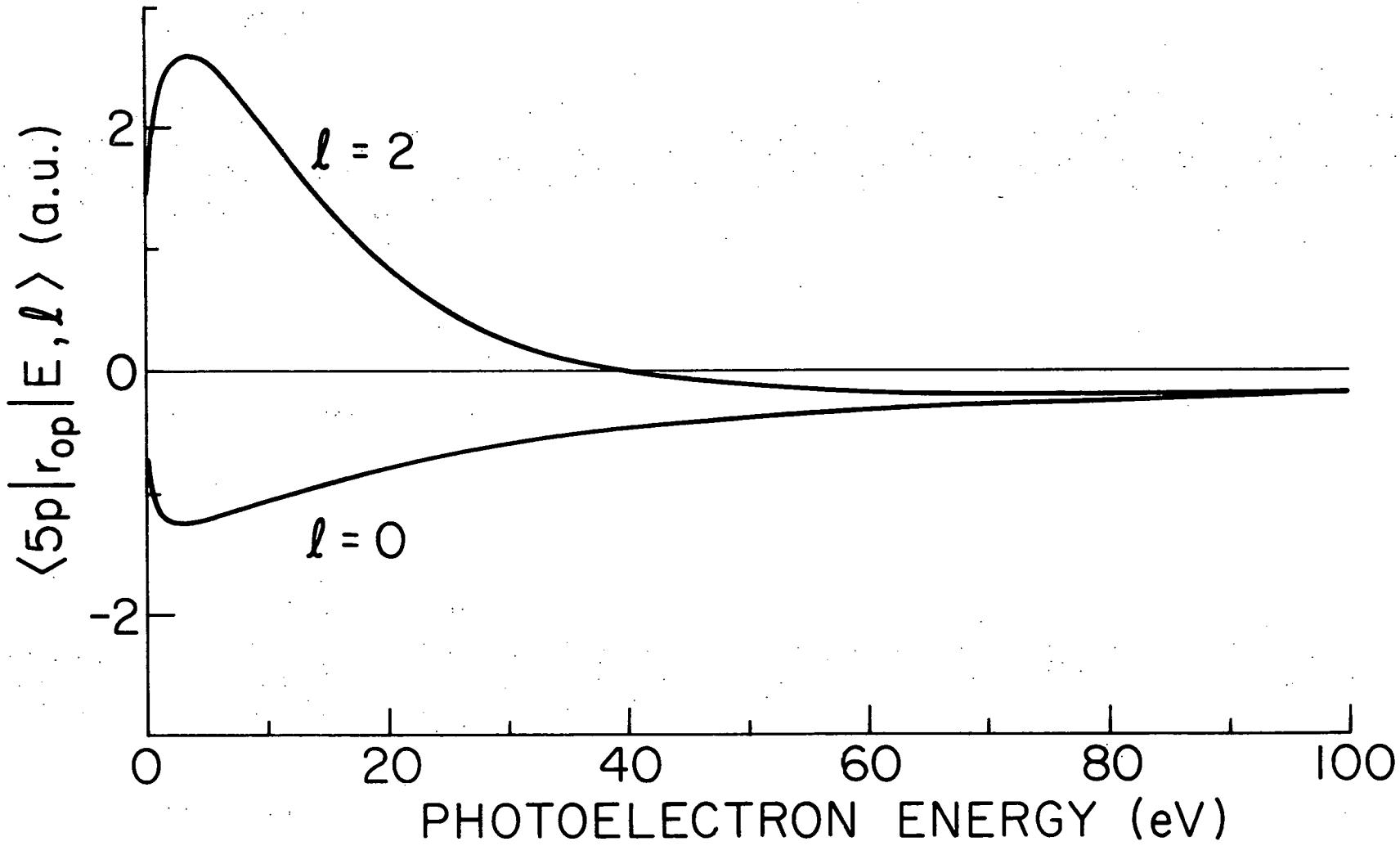
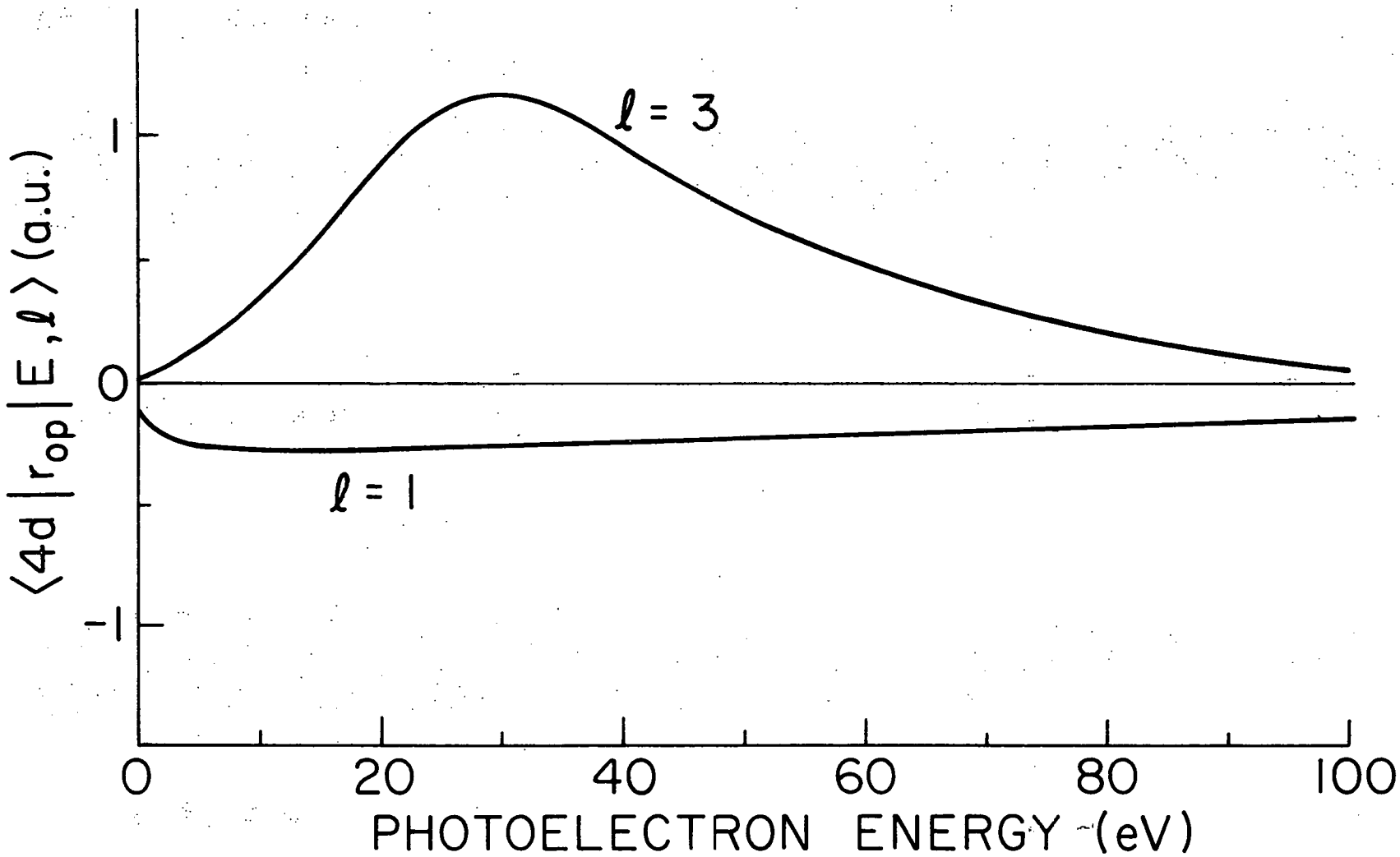

$\langle 5p | r_{op} | E, \ell \rangle$ (a.u.)
2
0
-2
$\ell = 2$
$\ell = 0$
0
20
40
60
80
100
PHOTOELECTRON ENERGY (eV)

Fig. 21. p- and f-wave dipole matrix elements for photoionization of the Xe 4d subshell.


$\langle 4d | r_{op} | E, \ell \rangle$ (a.u.)
1
0
-1
$\ell = 3$
$\ell = 1$
0
20
40
60
80
100
PHOTOELECTRON ENERGY (eV)

4d ionization. In fact, Amusia[9] has shown that interaction between the 4d and 5p electrons is responsible for the rapid increase in $\beta(E)$ in this region.

To include the effects of intershell correlations within the pseudopotential approach, we have extended the analysis of Cooper and Zare[12] to second order in the perturbing Hamiltonian (see Appendix C). In doing so, we reproduce equation (2) with the substitution $R_{\ell\pm1} \longrightarrow R^{eff}_{\ell\pm1}$ where the effective matrix element is given by

$$R^{eff}_{\ell\pm1} = R_{\ell\pm1} + \sum_{int} R_{int}(U^{Dir}_{int} - U^{Ex}_{int})/(\omega-\omega_{int} + i\eta). \qquad (19)$$

The sum here is over all intermediate states. R_{int} is the dipole matrix element for transition into the intermediate state, U^{Dir}_{int} (U^{Ex}_{int}) represents a direct (exchange) interaction with the intermediate state, ω is the photon energy, and ω_{int} is the excitation energy of the intermediate state. η is a small positive energy which indicates how the pole is to be treated. The precise forms of the components of equation (19) are given in Appendix C, and will not be repeated here. It suffices to note that intershell dynamic correlations modify both the phase and amplitude of the dipole matrix element. Carrying such a perturbation to all orders would reproduce the RPAE equations.

In assessing the effects of intershell correlations, we have first applied the pseudopotential method to the 4d and 5p shells independently, i.e., we have used the results of Section IV.B. The appropriate wavefunctions and matrix elements

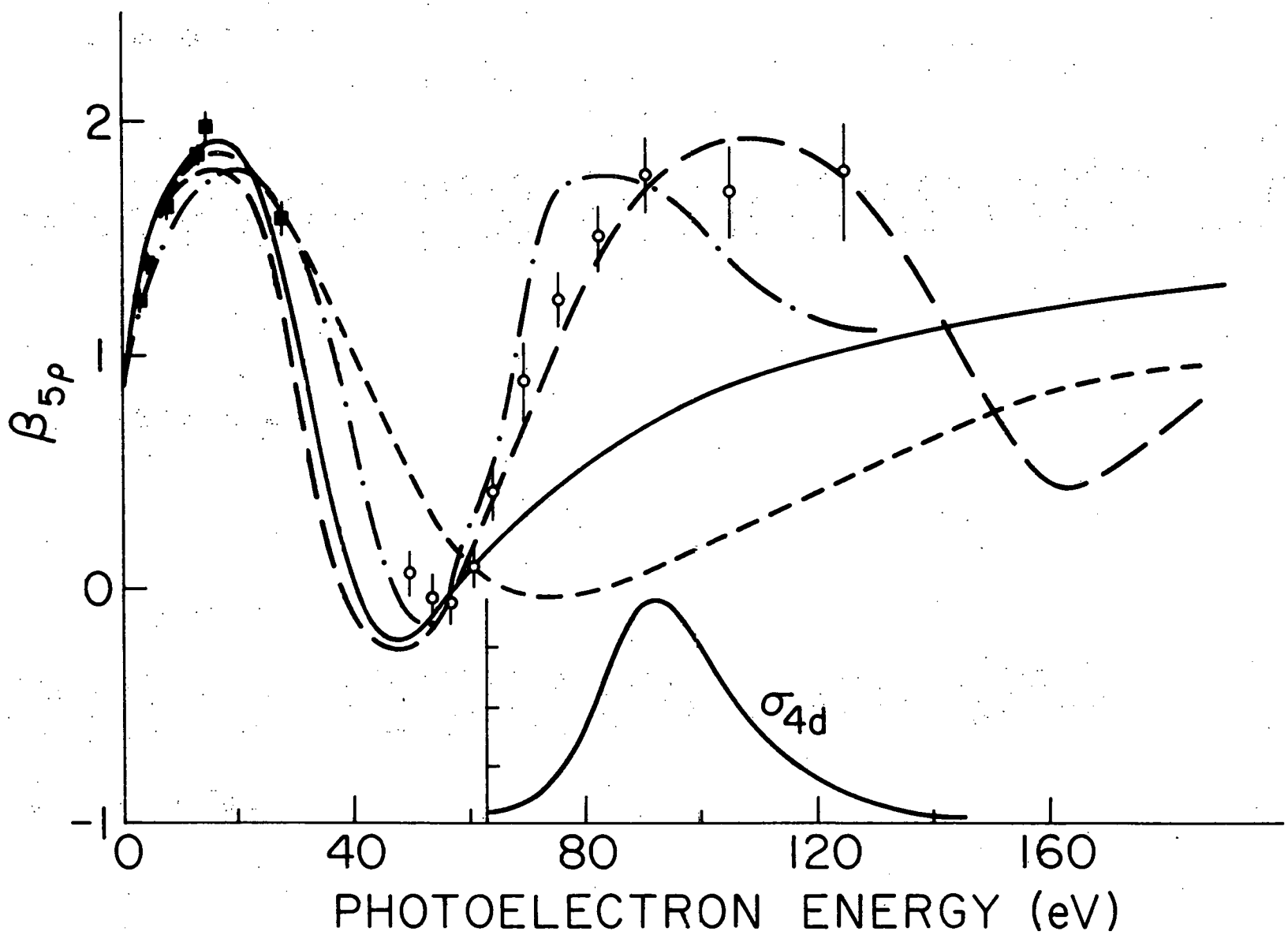
were then inserted into equation (19).

In performing the sum in equation (19), we have included only those intermediate states with a 4d hole and a continuum electron, neglecting contributions from bound intermediate states which contribute $\leq 10\%$ of the 4d oscillator strength. Although this may be of some consequence near threshold, it should not affect any qualitative conclusions drawn here.

The results of this analysis are shown in Figure 22, where we compare $\beta_{5p}^{calc}(E)$, both with and without 4d interactions, to the data (for emphasis, we also display σ_{4d} here). We see a remarkable improvement in the agreement of theory and data. This agreement could perhaps be improved by further adjustment of the 5p and/or 4d parameters.

The effect of intershell interactions is dominated (at least in the present case) by the "on shell" ($\omega = \omega_{int}$) terms of equation (19), which modify the phase of the $5p \longrightarrow E,d$ matrix element above the 4d threshold.

Fig. 22. Asymmetry parameter, $\beta(E)$, for photoionization of the Xe 5p subshell: —— (pseudopotential without 4d interactions); ——·—— (pseudopotential with 4d interactions); --- (RPAE without 4d interactions, Ref. 7); —— —— (RPAE with 4d interactions, Ref. 7). Inset shows Xe 4d photoionization cross section as determined by the pseudopotential analysis.


2
1
0
-1
β_{5p}
0
40
80
120
160
PHOTOELECTRON ENERGY (eV)
σ_{4d}

V. CONCLUSIONS

We have seen that the RPAE is in consistently better agreement with experiment than are HF calculations. This demonstrates the importance of intra-atomic electron-electron interactions in the photoionization spectra of rare gases. Further, the pseudopotential results are all consistent with the interpretation that intrashell correlations may be adequately included for a wide range of electron energies by the use of an appropriately optimized local pseudopotential.

If this interpretation is correct, we may take as a measure of the electron-electron correlations the difference between the pseudopotential and the corresponding Hartree potential. The current results then indicate that such effects are much less important in the photoionization of Ar 3s electrons than in the photoionization of Ar 3p electrons (see Figs. 7 and 9). This can be explained physically in terms of the photoionization cross section, which is an order of magnitude smaller in the former case than in the latter.

The atomic pseudopotentials have enjoyed considerable success in describing the photoionization of rare gases, providing accurate values of the photoionization cross sections, phase shifts, and angular distributions. We therefore suggest that the following questions be addressed in further studies: (i) How may the pseudopotential approach be adapted to the study of adsorbates on solid surfaces? (ii) What modifications must be made to treat photoionization of open shell atoms with

the pseudopotential method? (iii) Can accurate local potentials be obtained without the aid of experimental data?

APPENDIX A

DIPOLE SUM RULES

In this appendix we derive the f-sum rule, which is often regarded as equivalent to the statement that the solutions of the Schrödinger equation form a complete set. We also derive the corresponding result for Hartree-Fock functions and discuss its implications for continuum properties.

1. Sum rules for exact wavefunctions

Consider first the case of a one-electron system for which the Schrödinger equation is

$$H|\phi_n\rangle = E_n|\phi_n\rangle \tag{1}$$

where H is the (one-electron) Hamiltonian, and E_n is the energy of the state $|\phi_n\rangle$. We also have the following general relationships:

$$v_z = i[H,z] \tag{2}$$

$$[z,p_z] = i \tag{3}$$

where $p_z(v_z)$ is the z-component of the momentum (velocity) operator. For the one-electron system $p_z = v_z$ and we have

$$[z,[H,z]] = 1 \tag{4}$$

We now evaluate

$$<\phi_i|\phi_i> = <\phi_i|2zHz - z^2H - Hz^2|\phi_i>= 1. \tag{5}$$

By inserting a complete set of states and making use of equation (1) we obtain

$$2 \sum_k |<\phi_i|z|\phi_k>|^2(E_k-E_i) = 1. \tag{6}$$

With equation (2) this becomes

$$2 \sum_k |<\phi_i|p_z|\phi_k>|^2/(E_k-E_i) = 1. \tag{7}$$

If we define the oscillator strength for transitions from state $|\phi_i>$ to state $|\phi_k>$ as

$$f_{ik} \equiv |<\phi_i|\hat{d}|\phi_k>|^2 2/(E_k-E_i) \tag{8}$$

where the dipole operator is given in velocity form by

$$\hat{d}^V = ip_z$$

and in length form by

$$\hat{d}^L = [z,H].$$

Henceforth, superscripts L and V will denote length and

velocity forms, respectively. We may then rewrite equations (6) and (7) as

$$S_0^L \equiv \sum_k f_{ik}^L = 1 \tag{9}$$

and

$$S_0^V \equiv \sum_k f_{ik}^V = 1. \tag{10}$$

The subscript 0 here indicates that the sum rule applies to transitions between one-electron orbitals.

These results may be rewritten in terms of the photoionization cross section as (see reference 6 and Appendix B)

$$S_0^{L,V} = \sum_k{}' f_{ik} + \frac{1}{2\pi\alpha} \int_{I_i}^{\infty} \sigma(E)\,dE \tag{11}$$

where the sum here is over bound excited states, I_i is the ionization potential of state i, α is the fine structure constant and σ is the cross section.

For an N-electron system, the electromagnetic field couples to each electron and the respective dipole operators become

$$\hat{d}^V = i \sum_{n=1}^{N} P_{nz} \tag{12}$$

and

$$\hat{d}^L = \sum_{n=1}^{N} [z_n, H], \tag{13}$$

where the subscript n denotes the n-th electron. The result corresponding to equations (9) and (10) is then

$$S^L = \sum_k f^L_{ik} = N, \tag{14}$$

and

$$S^V = \sum_k f^V_{ik} = N, \tag{15}$$

where the oscillator strengths are now defined in terms of N-electron dipole operators and N-electron states. The sum is again over a complete set of states. Note that these results apply for transitions of the N-electron system to excited states, not to transitions of a given one-electron orbital.

To obtain these results it is sufficient that the solutions of the Schrödinger equation form a complete set and that the velocity and momentum operators coincide.

2. Sum rules for Hartree-Fock functions

The Hartree-Fock equation for a one-electron orbital ϕ_i may be written

$$(H_{loc} + V_{ex})\phi_i = \varepsilon_i \phi_i \tag{16}$$

where H_{loc} is the local portion of the Hamiltonian and satisfies

$[H_{loc},z] = ip_z$. V_{ex} is the exchange potential

$$V_{ex} = -\sum_{j=1}^{N} \langle\phi_j(\vec{r}')|\frac{1}{|\vec{r}-\vec{r}'|}|\phi_j(\vec{r})\rangle. \tag{17}$$

Note that this is not an inner product, rather matrix elements of V_{ex} are evaluated as

$$\langle\phi_a|V_{ex}|\phi_b\rangle$$
$$\equiv \sum_{j=1}^{N}\langle\phi_a(\vec{r})\phi_j(\vec{r}')||\vec{r}-\vec{r}'|^{-1}|\phi_j(\vec{r})\phi_b(\vec{r}')\rangle\delta_{s_a s_j}\delta_{s_j s_b} \tag{18}$$

where s_i is the spin projection of the i-th spin orbital.

We then have

$$v_z = p_z + i\sum_{j=1}^{N}\langle\phi_j(\vec{r}')|\frac{z-z'}{|\vec{r}-\vec{r}'|}|\phi_j(\vec{r})\rangle \tag{19}$$

and

$$[z,[H_{HF},z]] = 1 + \sum_{j=1}^{N}\langle\phi_j(\vec{r}')|\frac{(z-z')^2}{|\vec{r}-\vec{r}'|}|\phi_j(\vec{r})\rangle. \tag{20}$$

Analysis parallel to that of section 1 then leads to

$$S_0^L = 1 + \sum_{j=1}^{N}\langle\phi_i(\vec{r})\phi_j(\vec{r}')|\frac{(z-z')^2}{|\vec{r}-\vec{r}'|}|\phi_j(\vec{r})\phi_i(\vec{r}')\rangle\delta_{s_i s_j}$$

$$= 1 + \Delta S_0. \tag{21}$$

To evaluate the corresponding result for the velocity formalism we use equation (19) to write

$$\langle\phi_i|ip_z|\phi_k\rangle = \langle\phi_i|z|\phi_k\rangle(E_k-E_i)$$

$$+ \sum_{j=1}^{N} \langle\phi_i(\vec{r})\phi_j(\vec{r}')|\frac{z-z'}{|\vec{r}-\vec{r}'|}|\phi_j(\vec{r})\phi_k(\vec{r}')\rangle\delta_{s_i s_j}\delta_{s_j s_k}. \quad (22)$$

Squaring both sides, summing over k and using equation (8) then yields

$$S_0^V = 1 - \Delta S_0 + \sum_k \cdot$$

$$\cdot\left|\sum_{j=1}^{N} \langle\phi_i(\vec{r})\phi_j(\vec{r}')|\frac{z-z'}{|\vec{r}-\vec{r}'|}|\phi_j(\vec{r})\phi_k(\vec{r}')\rangle\delta_{s_i s_j}\delta_{s_j s_k}\right|^2, \quad (23)$$

which is the sum rule for transitions between one-electron HF orbitals.

Finally, if we use the N-electron dipole operator and N-electron HF wavefunctions, which are Slater determinants of one-electron HF spin orbitals, we obtain

$$S_{HF}^L = N + \sum_{j=1}^{N}\sum_{i=1}^{N} \langle\phi_i(\vec{r})\phi_j(\vec{r}')|\frac{(z-z')^2}{|\vec{r}-\vec{r}'|}|\phi_j(\vec{r})\phi_i(\vec{r}')\rangle\delta_{s_i s_j}$$

$$= N + \Delta S, \quad (24)$$

and

$$S_{HF}^{V} = N - \Delta S + \sum_{i=1}^{N} \sum_{k}{}' \frac{1}{(E_k - E_i)} \sum_{j=1}^{N} \langle \phi_i(\vec{r})\phi_j(\vec{r}\,')\left|\frac{z-z'}{|\vec{r}-\vec{r}\,'|}\right| \phi_j(\vec{r})\phi_k(\vec{r}\,')\rangle \cdot$$

$$\cdot\, \delta_{s_i s_j} \delta_{s_j s_k}{}^{2}, \tag{25}$$

where the primed sum is restricted by the Pauli principle to initially unoccupied orbitals.

In practice, the last term of equation (25) is small. We see immediately then that use of either the length or velocity form of the dipole operator with Hartree-Fock functions will yield inaccurate cross sections, but that use of an average of the two operators will nearly satisfy the exact sum rule.

APPENDIX B

THEORY OF PHOTOIONIZATION

In this appendix we develop the formalism used in Chapter Two. We seek to determine such properties as the atomic photoionization cross section, photoelectron phase shifts, dipole matrix elements, and photoelectron angular distributions. In short we wish to analyse the absorption of a photon by an atom.

For clarity, we will use the one-electron model, with generalization to many-electron systems being straightforward.

For a more detailed discussion of what follows, the reader is referred to standard quantum mechanics texts (cf. reference 31, Chapter XXI).

Classically, the Hamiltonian for an electron in the presence of an electromagnetic field is obtained from the field-free Hamiltonian by the substitution $\vec{p} \longrightarrow (\vec{p} - \frac{1}{c}\vec{A})$, where $\vec{p}$ is the electron momentum, c is the velocity of light, and $\vec{A}$ is the vector potential of the field. The kinetic energy term of the Hamiltonian then becomes

$$\frac{p^2}{2} \longrightarrow \frac{1}{2}(p^2 - \frac{1}{c}\vec{p}\cdot\vec{A} - \frac{1}{c}\vec{A}\cdot\vec{p} + (\frac{1}{c})^2 A^2), \tag{1}$$

so that the interaction of the electron with the field may be written

$$H_{int} = H_I + H_{II}$$

where

$$H_I = -\frac{1}{2c}(\vec{p}\cdot\vec{A}+\vec{A}\cdot\vec{p}), \tag{2}$$

$$H_{II} = \frac{1}{2c^2} A^2. \tag{3}$$

We now expand the vector potential $\vec{A}$ in quantized form;

$$\vec{A} = \sum_{\vec{k},\vec{\varepsilon}} \left(\frac{2\pi c^2}{L^3}\right)^{1/2} \left(a_{\vec{k},\vec{\varepsilon}}\vec{\varepsilon}e^{i\vec{k}\cdot\vec{r}}+a^+_{\vec{k},\vec{\varepsilon}}\vec{\varepsilon}e^{-i\vec{k}\cdot\vec{r}}\right) \tag{4}$$

where $a_{\vec{k},\vec{\varepsilon}}$ $(a^+_{\vec{k},\vec{\varepsilon}})$ is an annihilation (creation) operator for a photon of momentum $\vec{k}$, energy $\omega = kc$ and polarization vector $\vec{\varepsilon}$. The normalization is that for a system enclosed in a cube of volume L^3 with periodic boundary conditions, and it is understood that $L \longrightarrow \infty$ at the end of any calculation.

It can be shown that if $ka << 1$, where a is the radius of the atom, the transition is dominated by H_I. This condition is satisfied for photon energies less than a few hundred electron volts, well above the current range of interest. We therefore neglect H_{II} in what follows.

Substitution of equation (4) into equation (2) and making use of the transverse nature of the field $(\vec{k}\cdot\vec{\varepsilon}= 0)$, we obtain

$$H_I = -\sum_{\vec{k},\vec{\varepsilon}} \left(\frac{2}{\omega L^3}\right)^{1/2} \left(a_{\vec{k},\vec{\varepsilon}} e^{i\vec{k}\cdot\vec{r}}(\vec{\varepsilon}\cdot\vec{p}) + c.c.\right) \tag{5}$$

We wish to describe the process in which a photon of mementum $\vec{k}$ and polarization $\vec{\varepsilon}$ is absorbed. For convenience we take $\vec{\varepsilon} = \hat{z}$, a unit vector in the z-direction. The transition probability per unit time is given by the "golden rule" formula

$$W_{j \longrightarrow E} = 2\pi |\langle \phi_j | H_I(\vec{k},\hat{z}) \phi_E \rangle|^2 \rho(E), \tag{6}$$

where ϕ_j and ϕ_E are the initial and final electron states and $\rho(E)$ is the density of final states at energy E. Use of equation (5) then gives

$$W_{j \longrightarrow E} = \frac{(2\pi)^2 N}{\omega L^3} |\langle \phi_j | p_z | \phi_E \rangle|^2 \rho(E), \tag{7}$$

where we have set $e^{i\vec{k}\cdot r} = 1$ (recall that $ka << 1$), and N is the number of photons in the initial state. Finally, the cross section is given by

$$\sigma_{j \longrightarrow E} = \frac{W_{j \longrightarrow E}}{\text{incident flux}} = \frac{(2\pi)^2}{\omega c} |\langle \phi_j | p_z | \phi_E \rangle|^2 \rho(E), \tag{8}$$

or, since $[z,H] = ip_z$

$$\sigma_{j \longrightarrow E} = \frac{(2\pi)^2 \omega}{c} |\langle \phi_j | z | \phi_E \rangle|^2 \rho(E). \tag{9}$$

We now address the problem of photoionization. The final state in this process is that of an electron of momentum $\vec{k}$ and energy $\vec{E}$. Asymptotically, this takes the form of a plane wave of momentum $\vec{k}$ plus an incoming spherical wave:

$$\phi_E = 4\pi \sum_{\ell,m} (i)^{\ell} e^{-i\delta_\ell} Y^*_{\ell,m}(\hat{k}) Y_{\ell,m}(\hat{r}) g_{k\ell}(r), \tag{10}$$

where $Y_{\ell,m}$ is a spherical harmonic and δ_ℓ is a phase shift with respect to a free particle wavefunction. That this is the proper boundary condition can be seen from the following argument (cf. reference 32, Chapter 12 and reference 33).

Consider the scattering of an electron from a central potential. The state of the system before the collision is a wave packet moving toward the target. After the collision, the state contains the original packet, which has moved past the target, plus a scattered wave. In tracing the time-dependence of the collision one finds that the wavefunction is expressed as a superposition of plane waves plus outgoing spherical waves. The distinct character of the two regimes is accounted for by a difference in the phase relations of the component waves.

In the present case we have an electron of momentum $\vec{k}$ moving away from the origin. Since this is the time reverse of the collision process just described, the proper boundary conditions are those of a plane wave plus an incoming spherical wave.

Combining equations (9) and (10) we then have

$$\frac{d\sigma}{d\Omega} = \frac{4(2\pi)^4\omega}{c} \Big| \sum_{\ell',m'} (i)^{\ell'} e^{-i\delta_{\ell'}} Y^*_{\ell'm'}(\hat{k}) R_{\ell'} \cdot$$

$$\cdot \langle Y_{\ell,m}(\hat{r}) | \cos\theta | Y_{\ell',m'}(\hat{r}) \rangle \Big|^2 \rho(E) \tag{11}$$

where we have written $\phi_i = a_i(r) Y_{\ell,m}(\hat{r})$, and

$$R_{\ell'} = \int_0^\infty dr\, r^3\, a_i(r) g_{k\ell'}(r). \tag{12}$$

To evaluate this we note that

$$Y_{\ell,m}(\hat{r})\cos\theta = \left[\frac{(\ell+1+m)(\ell+1-m)}{(2\ell+1)(2\ell+3)}\right]^{1/2} Y_{\ell+1,m}(\hat{r})$$

$$+ \left[\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}\right]^{1/2} Y_{\ell-1,m}(\hat{r}) \tag{13}$$

and use the orthogonality properties of the spherical harmonics to obtain

$$\frac{d\sigma}{d\Omega} = \frac{4(2\pi)^4\omega}{c} \Big\{ \left[\frac{(\ell+1+m)(\ell+1-m)}{(2\ell+1)(2\ell+3)}\right] R_{\ell+1}^2 |Y_{\ell+1,m}|^2$$

$$+ \left[\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}\right] R_{\ell-1}^2 |Y_{\ell-1,m}|^2$$

$$- \left[\frac{(\ell+1+m)(\ell+1-m)}{(2\ell+1)(2\ell+3)}\right]^{1/2} \left[\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}\right]^{1/2} R_{\ell-1} R_{\ell+1} 2\cos(\delta_{\ell+1}-\delta_{\ell-1}) \cdot$$

$$\cdot Y^*_{\ell-1,m} Y_{\ell+1,m} \Big\} \rho(E). \tag{14}$$

We now assume uniform population of the magnetic sublevels and average over m. This is accomplished with the aid of the relations

$$\sum_m |Y_{\ell,m}|^2 = \frac{2\ell+1}{4\pi}, \tag{15}$$

and

$$\sum_m m^2 |Y_{\ell,m}|^2 = \frac{\ell(\ell+1)(2\ell+1)}{8\pi} \sin^2\theta, \tag{16}$$

as well as equation (13). As a result we obtain

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi)^3\omega}{(2\ell+1)^2 c}\{[2(\ell+1)^2-(\ell+1)(\ell+2)\sin^2\theta]R_{\ell+1}^2 + [2\ell^2-(\ell-1)\ell\sin^2\theta]R_{\ell-1}^2$$

$$-2\ell(\ell+1)[2-3\sin^2\theta]\cos(\delta_{\ell+1}-\delta_{\ell-1})R_{\ell+1}R_{\ell-1}\}\rho(E). \tag{17}$$

We may integrate this over angles to find the total cross section

$$\sigma = \frac{(2\pi)^4\omega}{(2\ell+1)c}\,\frac{4}{3}[\ell R_{\ell-1}^2+(\ell+1)R_{\ell+1}^2]\rho(E). \tag{18}$$

Inserting equation (18) into equation (17), we find

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}\,[1 + \beta P_2(\cos\theta)], \tag{19}$$

where $P_2(x) = (3x^2-1)/2$, and

$$\beta = \frac{\ell(\ell-1)R_{\ell-1}^2+(\ell+1)(\ell+2)R_{\ell+1}^2-6\ell(\ell+1)R_{\ell-1}R_{\ell+1}\cos(\delta_{\ell+1}-\delta_{\ell-1})}{(2\ell+1)[\ell R_{\ell-1}^2+(\ell+1)R_{\ell+1}^2]}. \tag{20}$$

This parameter β completely characterizes the angular distribution of photoemitted electrons.

We return now to the evaluation of the total cross section. If we wish to normalize the final state (equation (10)) to a plane wave of unit amplitude at $r = \infty$, the functions $g_{k\ell}(r)$ then behave asymptotically as

$$g_{k\ell}(r) \xrightarrow[r\to\infty]{} \frac{1}{kr}\sin(kr+\frac{1}{k}\ln(kr)-\ell\pi/2+\delta_\ell). \tag{21}$$

With this normalization, the density of final states is

$$\rho(E) = (2\pi)^{-3} \tag{22}$$

as appropriate for plane waves, and equation (18) becomes

$$\sigma = \frac{8\pi}{3}\frac{\omega}{(2\ell+1)c}[\ell R^2_{\ell-1}+(\ell+1)R^2_{\ell+1}] \tag{23}$$

for the cross section for emitting a single electron. This result should be multiplied by the number of electrons in the initial subshell to correspond to experiment.

APPENDIX C

INTERSHELL CORRELATIONS

In this appendix we develop the mechanism necessary to include intershell correlations. In the first part we follow reference 31. The latter part is basically due to Cooper and Zare.[12]

The Hamiltonian for a system of electrons in an electromagnetic field may be written

$$H = \sum_i T_i + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} + \sum_i (h_i a^+_{\vec{k},\vec{\varepsilon}} + h_i^* a_{\vec{k},\vec{\varepsilon}}) \tag{1}$$

where

$$T_i = \frac{p_i^2}{2} - \frac{Z}{r_i} \tag{2}$$

with p_i and r_i the momentum and position of the i-th electron. Z is the nuclear charge, h_i represents the interaction of the i-th electron with the field, and $a_{\vec{k},\vec{\varepsilon}}$ $(a^+_{\vec{k},\vec{\varepsilon}})$ is the annihilation (creation) operator for a photon of momentum $\vec{k}$ and polarization $\vec{\varepsilon}$.

We assume that the N-electron wavefunction may be written as a single Slater determinant of one-electron Hartree-Fock spin-orbitals

$$|\psi\rangle = \frac{1}{\sqrt{N}} \sum_p (-)^p \prod_{i=1}^{N} |\phi_i(r_i)\rangle, \tag{3}$$

where p is the permutation operator.

For excitation of an electron from a state $|\phi_1\rangle$ to a state $|\phi_2\rangle$ simultaneous with the absorption of a photon, we have as the first order matrix element

$$M_1 = \langle\Psi_f|H|\Psi_i\rangle = \langle\phi_2|h|\phi_1\rangle. \tag{4}$$

(We denote the N-electron function by Ψ, and one-electron orbitals by ϕ.)

Contributions to the transition amplitude which are second order in the Hamiltonian are

$$M_2 = \sum_{int} \frac{1}{E_{int}-E_i}\langle\Psi_f|H|\Psi_{int}\rangle\langle\Psi_{int}|H|\Psi_i\rangle \tag{5}$$

where $E_i(E_{int})$ is the total energy of the initial (intermediate) state and the sum is to be carried out over all intermediate states. Since the final state contains one less photon than the initial state, this reduces to

$$M_2 = \sum_{int} \frac{1}{E_{int}-E_i} [\langle\Psi_f|H^I|\Psi_{int}\rangle\langle\Psi_{int}|H^0|\Psi_i\rangle$$
$$+ \langle\psi_f|H^0|\psi_{int}\rangle\langle\psi_{int}|H^I|\psi_i\rangle] \tag{6}$$

where $H^I = a_{\vec{k},\vec{\varepsilon}} \sum_i h_i + a^+_{\vec{k},\vec{\varepsilon}} \sum_i h_i^*$ and $H^0 = H - H^I$.

The first term of equation (6) corresponds to the scattering of two electrons prior to absorption of the photon. We will argue later that this term is small and concentrate on the second term, which reduces to

$$M_2 = \sum_{j<F}{}' \sum_{i>F}{}' \frac{\langle\phi_i|h|\phi_j\rangle[\langle\phi_j\phi_2|\frac{1}{r_{12}}|\phi_i\phi_1\rangle-\langle\phi_j\phi_2|\frac{1}{r_{12}}|\phi_1\phi_i\rangle]}{\omega-(\varepsilon_i-\varepsilon_j)+i\eta} \tag{7}$$

where $\omega = \varepsilon_2-\varepsilon_1$ is the photon energy. The first sum is over initially unoccupied orbitals, the second sum is over occupied orbitals, and the term $j = 1$, $i = 2$ is to be excluded. The presence of the infinitesimal, $i\eta$, indicates how the pole is to be treated $(\eta \longrightarrow 0^+)$.

The total transition amplitude is then

$$\begin{aligned} M &= M_1 + M_2 \\ &= \langle\phi_2|h|\phi_1\rangle + \sum_{j<F}{}' \sum_{i>F}{}' \frac{\langle\phi_i|h|\phi_j\rangle[\langle\phi_j\phi_2|\frac{1}{r_{12}}|\phi_i\phi_1\rangle-\langle\phi_j\phi_2|\frac{1}{r_{12}}|\phi_1\phi_i\rangle]}{\omega - (\varepsilon_i-\varepsilon_j) + i\eta} \\ &= D^0 + D^{dir} - D^{ex}. \end{aligned} \tag{8}$$

Using the dipole operator for a photon polarized in the z-direction $(h \propto z)$ we evaluate D^0 as

$$D^0 = AR_{12}[(2\ell_1+1)(2\ell_2+1)]^{1/2}(-)^{m_2} \begin{matrix} \ell_2 & 1 & \ell_1 \\ -m_2 & 0 & m_1 \end{matrix} \begin{matrix} \ell_2 & 1 & \ell_1 \\ 0 & 0 & 0 \end{matrix} \tag{9}$$

where A contains all the constant factors which are common to D^0, D^{dir}, and D^{ex}, and

$$R_{12} = \int_0^\infty dr\, rP_1(r)P_2(r). \tag{10}$$

Properties of the 3-j symbols are discussed in reference 34.

$P_i(r)$ is defined by

$$\phi_i(r) = Y_{\ell_i,m_i}(\hat{r})P_i(r)/r. \tag{11}$$

The direct and exchange terms can be similarly evaluated as

$$D_{ji}^{dir} = \langle\phi_i|h|\phi_j\rangle\langle\phi_j\phi_2|\frac{1}{r_{12}}|\phi_i\phi_1\rangle$$

$$= AR_{ji}[(2\ell_j+1)(2\ell_i+1)]^{1/2}(-)^{m_j}\begin{pmatrix}\ell_j & 1 & \ell_i\\ -m_j & 0 & m_i\end{pmatrix}\begin{pmatrix}\ell_j & 1 & \ell_i\\ 0 & 0 & 0\end{pmatrix}\cdot$$

$$\sum_{\ell',m'}\Bigg\{I_{\ell'}(j,2,i,j)[(2\ell_j+1)(2\ell_1+1)(2\ell_1+1)(2\ell_2+1)]^{1/2}\cdot$$

$$\cdot\begin{pmatrix}\ell_i & \ell' & \ell_j\\ -m_i & -m' & m_j\end{pmatrix}\begin{pmatrix}\ell_i & \ell' & \ell_j\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & \ell' & \ell_1\\ -m_2 & m' & m_1\end{pmatrix}\begin{pmatrix}\ell_2 & \ell' & \ell_1\\ 0 & 0 & 0\end{pmatrix}\Bigg\} \tag{12}$$

where

$$I_{\ell'}(j,2,i,1) = \int_0^\infty dr_1dr_2P_j(r_1)P_2(r_2)P_i(r_1)P_1(r_2)r_<^{\ell'}/r_>^{\ell'+1} \tag{13}$$

and

$$D_{ji}^{ex} = \langle\phi_j|h|\phi_i\rangle\langle\phi_j\phi_2|\frac{1}{r_{12}}|\phi_1\phi_i\rangle$$

$$= AR_{ji}[(2\ell_j+1)(2\ell_i+1)]^{1/2}(-)^{m_j}\begin{pmatrix}\ell_j & 1 & \ell_i\\ -m_j & 0 & m_i\end{pmatrix}\begin{pmatrix}\ell_j & 1 & \ell_i\\ 0 & 0 & 0\end{pmatrix}\cdot$$

$$\cdot\sum_{\ell',m'} I_{\ell'}(2,i,j,j)(-)^{m_i+m_2+m'}\cdot$$

$$\cdot[(2\ell_1+1)(2\ell_2+1)(2\ell_i+1)(2\ell_j+1)]^{1/2}\cdot$$

$$\cdot\begin{pmatrix}\ell_i & \ell' & \ell_1\\ -m_i & -m' & m_1\end{pmatrix}\begin{pmatrix}\ell_i & \ell' & \ell_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & \ell' & \ell_j\\ -m_2 & m' & m_j\end{pmatrix}\begin{pmatrix}\ell_2 & \ell' & \ell_j\\ 0 & 0 & 0\end{pmatrix} \quad (14)$$

These equations may be reduced by summing over m', m_i, and m_j to obtain

$$D^{dir}_{\ell_j\ell_i} = AR(2\ell_j+1)(2\ell_i+1)[(2\ell_1+1)(2\ell_2+1)]^{1/2}(-)^{m_2}\cdot$$

$$\cdot\frac{1}{3}I_1(i,2,j,1)\begin{pmatrix}\ell_i & 1 & \ell_j\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix}\ell_2 & 1 & \ell_1\\ -m_2 & 0 & m_1\end{pmatrix}\begin{pmatrix}\ell_2 & 1 & \ell_1\\ 0 & 0 & 0\end{pmatrix} \quad (15)$$

and

$$D^{ex}_{\ell_j\ell_i} = AR_{ij}(2\ell_i+1)(2\ell_j+1)[(2\ell_1+1)(2\ell_2+1)]^{1/2}(-)^{m_2}\cdot$$

$$\cdot\sum_{\ell'}\left[I_{\ell'}(i,2,1,j)(-)^{\ell'+\ell_i+\ell_j}\begin{Bmatrix}\ell_2 & \ell_1 & 1\\ \ell_i & \ell_j & \ell'\end{Bmatrix}\cdot\right.$$

$$\left.\cdot\begin{pmatrix}\ell_2 & \ell_1 & 1\\ -m_2 & m_1 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & \ell_1' & \ell_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_i & \ell' & \ell_j\\ 0 & 0 & 0\end{pmatrix}\right] \quad (16)$$

Finally, we may write the transition amplitude as

$$M = AR^{eff}[(2\ell_1+1)(2\ell_2+1)]^{1/2}(-)^{m_2}\begin{pmatrix}\ell_2 & 1 & \ell_1\\ -m_2 & 0 & m_1\end{pmatrix}\begin{pmatrix}\ell_2 & 1 & \ell_1\\ 0 & 0 & 0\end{pmatrix} \quad (17)$$

where

$$R^{eff} = R_{12} + \sum_{j<F}{}' \sum_{i>F}{}' R_{ij}(2\ell_i+1)(2\ell_j+1)\cdot$$

$$\cdot[\tfrac{2}{3}I_1(i,2,j,1)\begin{pmatrix}\ell_j & 1 & \ell_i\\ 0 & 0 & 0\end{pmatrix}^2 - \sum_{\ell'}(-)^{\ell'+(\ell_1+\ell_2+\ell_1)\ell_j)/2}\cdot$$

$$\cdot I_{\ell'}(i,2,1,j)\left[\frac{(\ell_1+\ell_2+2)(\ell_1+\ell_2)(\ell_i+\ell_j+1)}{(\ell_i+\ell_j+2)(\ell_i+\ell_j)(\ell_1+\ell_2+1)}\right]^2\cdot$$

$$\cdot\begin{Bmatrix}1 & \ell_1 & \ell_2\\ \ell' & \ell_j & \ell_j\end{Bmatrix}\begin{pmatrix}\ell_i & \ell' & \ell_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & \ell' & \ell_j\\ 0 & 0 & 0\end{pmatrix}\cdot$$

$$\cdot(\omega-\varepsilon_j+\varepsilon_i+i\eta)^{-1} \tag{18}$$

a factor of 2, arising from a sum over spins of the intermediate states, has been included in D^{dir}. This factor does not occur in the exchange term since the spin of ϕ_j and ϕ_i is fixed by ϕ_1 and ϕ_2.

By writing the transition amplitude as in equation (17), we see immediately that the results of Appendix B hold with the substitution $R \longrightarrow R^{eff}$.

In arriving at these results, we have made several simplifying assumptions. Firstly, we have assumed orthogonal one-electron orbitals. For the calculations of this chapter this is not strictly true as we have used Hartree-Fock orbitals in the initial state. This introduces terms proportional to $\langle\phi_i|\phi_j\rangle$ into equation (7), where ϕ_j is an initial state orbital and ϕ_i is an excited orbital. We argue that these terms are small, since an expansion of continuum pseudopotential functions would involve principally continuum Hartree-Fock

functions. Secondly, we have neglected the first term of equation (6). This term consists entirely of virtual transitions, which in the present case were found to be much less important than real transitions. In fact, the neglected terms must be smaller than the retained virtual terms due to a larger energy denominator. Thirdly, we have assumed the atom to contain only closed shells. Otherwise, sums over m_i in equation (12) and (14) are not readily performed.

Appendix D

LISTING OF PHOTOIONIZATION PROGRAMS

1. Sample main program
2. Subroutines for calculating asymmetry parameters and cross sections
3. Subroutine for calculating Coulomb functions

1. Sample main program

```
C      SAMPLE MAIN PROGRAM FOR CALCULATING ASYMMETRY PARAMETERS.
C              CALLS SUBROUTINES CSETUP AND BETAC.
       DIMENSION WAVEB(200),WAVEC(200)
       DIMENSION CPOT(3)
       DIMENSION ENC(40)
       DIMENSION RDIRON(200,2,40),REXON(200,2,2,40),RTVON(2,40),
      1R2DIR(200,2,40),R2EX(200,2,2,40),RTV(2,40)
       DIMENSION XEN(35),BETA(35),FM(35),FP(35),DFM(35),DFP(35),GM(35)
      1,GP(35),DGM(35),DGP(35),FASDIF(35),RRCM(35),RRCP(35),PHAS1(35),
      2XSECL(35),PHAS2(35),RMAT(35),RMATM(35),RICM(35),RICP(35)
       COMMON/SETUP/ENC,RDIRON,REXON,RTVON,R2DIR,R2EX,RTV,NSTEP
       COMMON/APARAM/C,D,RB,A,B
       COMMON/XSEC/ECORE
       COMMON/PARAM/Q,DL
       DATA EO/0.01E00/
       CALL OPCLS(0)
       Q=FLOAT(54)
       READ(21,10) LO,N,LC,NC,NPTS,NDATA,NSTEP,ENSTEP,STEP
      1,(CPOT(I),I=1,3),CC,DD,RRB,EDIFF,(XEN(I),I=1,NDATA)
   10  FORMAT(7I5,/2F14.7,/3F14.7,/3F14.7,/F14.7,/(F14.7))
       WRITE(22,20)LO,N,LC,NC,NPTS,NDATA,NSTEP,ENSTEP,STEP
      1,(CPOT(I),I=1,3),CC,DD,RRB,EDIFF,(XEN(I),I=1,NDATA)
   20  FORMAT(7I5,/2F14.7,/3F14.7,/3F14.7,/F14.7,/(F14.7))
       ECORE=-2.7780
       CALL CSETUP(NPTS,WAVEB,WAVEC,R2EX,R2DIR,RTV,ENC,NDATA,
      1NSTEP,LO,N,LC,NC,EO,ENSTEP,STEP,XEN,EDIFF,RDIRON,REXON,RTVON,
      2CPOT)
    1  CONTINUE
       C=CC
       D=DD
       RB=RRB
       ECORE=-2.7780
       CALL BETAC(BETA,PHAS1,NDATA,NPTS,XEN,LO,N,FASDIF,RRCM,RRCP,
      1RMAT,RMATM,RICM,RICP,XSECL,PHAS2,FM,FP,DFM,DFP,GM,GP,
      2DGM,DGP,2,1)
    3  CONTINUE
       WRITE(22,30) ((XEN(I),RMATM(I),RMAT(I),FASDIF(I),BETA(I),XSECL
      1(I)),I=1,NDATA)
   30  FORMAT(1H1,T10,'ENERGY',T25,'R(L-1)',T40,'R(L+1)',T55,'DELTA',
      1T70,'BETA',T85,'CROSS SECTION',/T10,6('-'),T25,6('-'),T40,6(
      2'-'),T55,5('-'),T70,4('-'),T85,13('-'),/(T4,6F15.7))
    4  CONTINUE
       WRITE(22,40) ((XEN(I),RMATM(I),RRCM(I),RICM(I),RMAT(I),
      1RRCP(I),RICP(I)),I=1,NDATA)
   40  FORMAT (1H1,T10,'ENERGY',T25,'R(L-1)',T40,'RE(R-CORR)',
      1T55,'IM(R-CORR)',T70,'R(L+1)',T85,'RE(R-CORR)',T100,
      2'IM(R-CORR)',/T10,6('-'),T25,6('-'),T40,10('-'),T55,10('-'),
      5T70,6('-'),T85,10('-'),T40,10('-'),/(T4,7F15.7))
       WRITE(22,50) ((XEN(I),FASDIF(I),PHAS1(I),PHAS2(I)),I=1,NDATA)
   50  FORMAT(1H1,T10,'ENERGY',T25,'DELTA',T40,'DELTA-C(L-1)',
      1T55,'DELTA-C(L+1)',/T10,6('-'),T25,4('-'),T40,12('-'),T55,
      212('-'),/(T2,4F15.4))
       CALL OPCLS(1)
       STOP
       END
```

```
      SUBROUTINE OPCLS(K)
C       THIS SUBROUTINE OPENS AND CLOSES FILES.
      IF(K.EQ.1) GO TO 1
      OPEN(UNIT=22,DEVICE='DSK',FILE='OUT.DAT')
      OPEN(UNIT=21,DEVICE='DSK',FILE='XE4D.DAT')
      OPEN(UNIT=25,DEVICE='DSK',FILE='DMXBGR.DAT')
      OPEN(UNIT=24,DEVICE='DSK',FILE='CLXE.DAT')
      OPEN(UNIT=30,DEVICE='DSK',FILE='CLXEO.DAT')
      RETURN
    1 CLOSE(UNIT=22)
      CLOSE(UNIT=21)
      CLOSE(UNIT=25)
      CLOSE(UNIT=24)
      CLOSE(UNIT=30)
      RETURN
      END
```

2. Subroutines for calculating asymmetry parameters, and cross sections

```
      SUBROUTINE BETAC(BETA,PHAS1,NBETA,NPTS,XEN,LO,N,
     1FASDIF,RRCM,RRCP,RMAT,RMATM,RICM,RICP,
     1XSECL,PHAS2,FM,FP,DFM,DFP,GM,GP,DGM,DGP,ISET,IPSET)
C     CALCULATES BETA FOR POTENTIAL GIVEN IN U(X)
C     VARIABLES:
C        BETA=ARRAY(NBETA):ASSYMETRY PARAMETER USING
C     (LENGTH + VELOCITY)/2 FORMALISM
C        PHAS1=ARRAY(NBETA):SERVES AS DUMMY ARRAY;
C     UPON EXIT THIS ARRAY CONTAINS PHASE SHIFTS OF LO-1 WAVES.
C        PHAS2=ARRAY(NBETA):SERVES AS DUMMY ARRAY;
C     UPON EXIT THIS ARRAY CONTAINS PHASE SHIFTS OF LO+1 WAVES.
C     FORM OF DIPOLE OPERATOR
C        NBETA=NUMBER OF ENERGY POINTS AT WHICH BETA IS CALCULATED
C        NPTS=NUMBER OF POINTS IN CONTINUUM WAVEFUNCTIONS
C        XEN=ARRAY(NBETA):ENERGIES AT WHICH BETA IS CALCULATED
C        LO=ORBITAL QUANTUM NUMBER OF BOUND ELECTRON
C        N=PRINCIPLE QUANTUM NUMBER OF BOUND ELECTRON
C        FASDIF=ARRAY(NBETA):DIFFERENCE OF LO+1 AND LO-1 PHASE SHIFTS
C        RMAT=ARRAY(NBETA):DIPOLE MATRIX ELEMENT FOR N,LO-->E,LO+1
C     TRANSITIONS
C        RMATM=ARRAY(NBETA):DIPOLE MATRIX ELEMENT FOR N,LO-->E,LO-1
C     TRANSITIONS
C        RRCM=ARRAY(NBETA):REAL PART OF CORRELATION CONTRIBUTION TO
C     LO-1 TRANSITION MATRIX ELEMENT.
C        RRCP=ARRAY(NBETA):REAL PART OF CORRELATION CONTRIBUTION TO
C     LO+1 TRANSITION MATRIX ELEMENT.
C        RICM=ARRAY(NBETA):IMAGINARY PART OF CORRELATION CONTRIBUTION
C     TO LO-1 TRANSITION MATRIX ELEMENT.
C        RICP=ARRAY(NBETA):IMAGINARY PART OF CORRELATION CONTRIBUTION
C     TO LO+1 MATRIX ELEMENT.
C        XSECL=ARRAY(NBETA):PARTIAL CROSS-SECTION IN (L+V)/2 FORM
C        FM=ARRAY(NBETA):REGULAR COULOMB FUNCTION F(LO-1)
C        FP=ARRAY(NBETA);REGULAR COULOMB FUNCTION F(LO+1)
C        DFM=ARRAY(NBETA):DERIVATIVE OF FM ABOVE
C        DFP=ARRAY:DERIVATIVE OF FP ABOVE
C        GM,GP,DGM,DGP:SAME AS FM,FP,DFM,DFP FOR IRREGULAR COULOMB
C     FUNCTIONS
C        ISET: IF MATRIX ELEMENTS AND ASYMMETRY PARAMETERS ARE
C    NOT NEEDED ISET SHOULD BE SET TO ZERO
C       IPSET: IF A NEW POTENTIAL U(X) IS TO BE CALCULATED,
C     IPSET SHOULD BE NON-ZERO
C        LV=ORBITAL QUANTUM NUMBER OF SECOND SUBSHELL;
C     USED BY SUBROUTINE CORR; CURRENTLY SET WITH DATA STATEMENT
C        DIFFE=ENERGY DIFFERENCE OF FIRST AND SECOND ORBITALS;
C     USED BY CORR; CURRENTLY SET WITH DATA STATEMENT
C     SUBROUTINES USED-----------------------------------------
C     FUNCTION SUBROUTINES:
C        GRAND:  CALCULATES INTEGRAND OF DIPOLE-LENGTH MATRIX ELEMENT
C        GRANDV:  CALCULATES INTEGRAND OF DIPOLE-VELOCITY
C     MATRIX ELEMENT
C        U:  CALCULATES L=0 POTENTIAL
C     NORMAL SUBROUTINES:
C        SIMPSON:  INTEGRATES VIA SIMPSON'S RULE
C        PHASE:  CALCULATES PHASE SHIFTS OF CONTINUUM WAVEFUNCTIONS
C     BY MATCHING TO COULOMB WAVES AT LARGE RADIUS
```

```
C         CORR:  COMPUTES CORRELATION CONTRIBUTIONS TO TRANSITION
C      MATRIX ELEMENTS
C      ***************************************************************
       DIMENSION RCOM(200),RCOP(200)      !7/18/78
       DIMENSION A(20),RCO(200),DRCO(200)
       DIMENSION XEN(NBETA),BETA(NBETA),UU(210)
       DIMENSION FM(NBETA),FP(NBETA),DFM(NBETA),DFP(NBETA)
       DIMENSION GM(NBETA),GP(NBETA),DGM(NBETA),DGP(NBETA)
       DIMENSION FASDIF(NBETA),RRCM(NBETA),RRCP(NBETA)
       DIMENSION PHAS1(NBETA),XSECL(NBETA),PHAS2(NBETA),
      1RMAT(NBETA),RMATM(NBETA),RICM(NBETA),RICP(NBETA)
       EXTERNAL GRANDV
       COMMON/DWAV/LM,L
       EXTERNAL GRAND
       COMMON/DNUM/ZERO,ONE,TWO,THREE,FOUR
       COMMON/PII/PI
       COMMON/PARAM/Q,DL
       COMMON/WAVES/RCO,IGRAND,NN,LL
       COMMON/XSEC/ECORE
       COMMON/SET/RCOM,RCOP,CLM,CLP      !7/18/78
       DATA TENTH/.1E0/
       DATA PI/3.14159265358979 3E+00/
       DATA XSECX/3.4236579E 00/
       DATA ZERO,ONE,TWO,THREE,FOUR,FIVE,SIX,TWELVE/
      10.E0,1.E0,2.E0,3.E0,4.E0,5.E0,6.E0,12.E0/
C      **********************
       DATA LV,DIFFE/2,-2.32081/
C      **********************
       DATA STEP/0.05E0/
       IF(IPSET.EQ.0) GO TO 10     !7/18/78
       MAXU=NPTS+10
       DLO=FLOAT(LO)
       IGRAND=0
       NN=N
       LL=LO
       DO 170 I=1,10
  170  UU(I)=U(FLOAT(I)*TENTH*TENTH)
       DO 180 I=11,MAXU
  180  UU(I)=U(FLOAT(I-10)*STEP)
   10  CONTINUE      !7/18/78
       DO 632 II=1,NBETA
       III=II
       LM=LO-1
       LP=LO+1
       EN=XEN(II)
       ENT=EN+DIFFE
       DO 631 L=LM,LP,2
       INUM=0
       H=TENTH**2
       HH=H*H
       NMAX=10
       X=H
       XP=H+H
       P=ZERO
       PP=ZERO
```

```
C  ********************
C     SET UP POWER SERIES FOR INITIAL POINTS
C  ********************
      DL=FLOAT(L)
      ALPH1=-Q
      ALPH2=ZERO
      ALPH3=ZERO
      A(L+1)=ONE
      A(L+2)=TWO*ALPH1/FLOAT(2*L+2)
      A(L+3)=TWO*(ALPH1*A(L+2)+ALPH2-EN)/FLOAT(2*(2*L+3))
      LPONE=L+1
      LPFOUR=L+4
      LPTEN=L+10
      DO 11 I=LPFOUR,LPTEN
      DK=FLOAT(I)
      A(I)=(ALPH1*A(I-1)+(ALPH2-EN)*A(I-2)+ALPH3*A(I-3))
     1*TWO/((DK+DL)*(DK-DL-ONE))
   11 CONTINUE
      DO 12 I=LPONE,LPTEN
      P=P+A(I)*X**I
      PP=PP+A(I)*XP**I
   12 CONTINUE
      RCO(1)=P
      RCO(2)=PP
  201 UO=UU(INUM+1)-TWO*EN+(DL*DL+DL)/X**2
      UP=UU(INUM+2)-TWO*EN+(DL*DL+DL)/XP**2
      DO 200 ND=3,NMAX
      XM=X
      X=XP
      XP=XP+H
      UM=UO
      UO=UP
      UP=UU(INUM+ND)-TWO*EN+(DL*DL+DL)/XP**2
      PM=P
      P=PP
      PP=((TWO+FIVE*UO*HH/SIX)*P-(ONE-UM*HH/TWELVE)*PM)
     1/(ONE-UP*HH/TWELVE)
      DRCO(ND-1)=(PP*(ONE-HH*UP/SIX)-PM*(ONE-HH*UM/SIX))/(TWO*H)
      RCO(ND)=PP
  200 CONTINUE
      IF(INUM.EQ.10) GO TO 203
      INUM=10
      RCO(1)=RCO(5)
      RCO(2)=RCO(10)
      DRCO(1)=DRCO(5)
      DRCO(NPTS)=ZERO
      H=STEP
      HH=H*H
      X=H
      XP=H+H
      NMAX=NPTS
      P=RCO(1)
      PP=RCO(2)
      GO TO 201
  203 CONTINUE
```

```
      IF(ISET.EQ.0) GO TO 20      !7/18/78
      CALL SIMPSN(STEP,XP,GRAND,VALUE)
   20 CONTINUE      !7/18/78
      CALL SIMPSN(STEP,XP,GRANDV,VMAT)
      IGRAND=1
      IF(L.EQ.LP) GO TO 631
      RM=RCO(NPTS-1)
      DRM=DRCO(NPTS-1)
      IF(ISET.NE.0) GO TO 666      !7/18/78
      BETA(1)=VMAT                                  !7/18/78
      DO 40 J=1,NPTS      !7/18/78
   40 RCOM(J)=RCO(J)      !7/18/78
      GO TO 631      !7/18/78
  666 CONTINUE
      RMATM(II)=VALUE
      RICM(II)=VMAT
C     ***********************7/18/78*******************************
      CALL CORR(CORRM,CORRA,RCO,ONE,NPTS,STEP,EN,ENT,LO,LV,LM,
     1DIFFE,II)
      CORR1=-PI*CORRA
      RQS=(RMATM(II)+RICM(II)/(XEN(II)-ECORE))/TWO
      RQS=RQS+CORRM
      PHASE1=ATAN2(CORR1,RQS)
  631 CONTINUE
C     ***********************7/18/78*****************************
      RP=RCO(NPTS-1)
      DRP=DRCO(NPTS-1)
      IF (ISET.NE.0) GO TO 50      !7/18/78
      PHAS1(1)=VMAT                !7/18/78
      DO 60 J=1,NPTS      !7/18/78
   60 RCOP(J)=RCO(J)      !7/18/78
      GO TO 30      !7/18/78
   50 CONTINUE      !7/18/78
      RMAT(II)=VALUE
      RICP(II)=VMAT
C     ***********************7/18/78*******************************
      CALL CORR(CORRP,CORRA,RCO,ONE,NPTS,STEP,EN,ENT,LO,LV,LP,
     1DIFFE,II)
      CORR2=-PI*CORRA
      RQSP=(RMAT(II)+RICP(II)/(XEN(II)-ECORE))/TWO
      RQSP=RQSP+CORRP
      PHASE2=ATAN2(CORR2,RQSP)
C     ***********************7/18/78****************************
   30 CONTINUE      !7/18/78
      CALL PHASE(EN,LO,ONE,NPTS,STEP,RM,DRM,RP,DRP,DELTA,CLM,CLP
     1,FM(II),FP(II),DFM(II),DFP(II),GM(II),GP(II),DGM(II),DGP(II))
      IF (ISET.EQ.0) RETURN      !7/18/78
      FASDIF(II)=DELTA
      FASDIF(II)=DELTA+PHASE2-PHASE1
      RMATM(II)=RMATM(II)/CLM
      RICM(II)=RICM(II)/CLM
      RMAT(II)=RMAT(II)/CLP
      RICP(II)=RICP(II)/CLP
C     ****************AVERAGING LENGTHAND VELOCITY***********
      RMAT(II)=(RMAT(II)+RICP(II)/(XEN(II)-ECORE))/TWO
```

```
      RMATM(II)=(RMATM(II)+RICM(II)/(XEN(II)-ECORE))/TWO
C     ***********************END AVERAGING ********************
      CORR1=CORR1/CLM
      CORR2=CORR2/CLP
      RQS=RQS/CLM                          !7/18/78
      RQSP=RQSP/CLP                        !7/18/78
      RMAT(II)=SQRT(RQSP**2+CORR2**2)          !7/18/78
      RMATM(II)=SQRT(RQS**2+CORR1**2)             !7/18/78
      RRCM(II)=RMAT(II)/RMATM(II)
      BETA(II)=(DLO*(DLO-ONE)/RRCM(II)+(DLO+ONE)*(DLO+TWO)*RRCM(II)
     1-SIX*DLO*(DLO+ONE)*COS(FASDIF(II)))/
     2((TWO*DLO+ONE)*(DLO/RRCM(II)+(DLO+ONE)*RRCM(II)))
      PHAS1(II)=PHASE1
      PHAS2(II)=PHASE2
      RICM(II)=CORR1
      RICP(II)=CORR2
      RRCM(II)=CORRM/CLM
      RRCP(II)=CORRP/CLP
C     **********THE FOLLOWING STATEMENTS CALCULATE XSECTIONS***
      XSECL(II)=XSECX*((EN-ECORE)/SQRT(TWO*EN))*(RMATM(II)
     1**2*FLOAT(LO)+FLOAT(LO+1)*RMAT(II)**2)
C     ***********
C     WRITE(200,642) EN,RMATM(II),RMAT(II),CLM,CLP
C     WRITE(108,642) EN,RMATM(II),CORR1,RMAT(II),CORR2,FASDIF(II)
C    1,PHASE2,PHASE1
  632 CONTINUE
      RETURN
      END
C
C
C
      SUBROUTINE  READ
C      THIS SUBROUTINE READS ATOMIC ORBITAL PARAMETERS.
      COMMON/GAM/GAMMA(11)
      COMMON/UPARAM/C(5,3,12),KK(3,11),ZETA(3,11),IREAD
      READ(25,68) ((KK(I,J),ZETA(I,J),J=1,11),I=1,3)
      READ(25,69) (((C(I,J,K),K=1,12),I=J,5),J=1,3)
      IREAD=1
   68 FORMAT(I2,F12.7)
   69 FORMAT(6F10.5)
      GAMMA(1)=1.E0
      DO 21 I=1,10
   21 GAMMA(I+1)=GAMMA(I)*FLOAT(I)
      RETURN
      END
C
C
C
      REAL FUNCTION U(X)
C      THIS SUBROUTINE CALCULATES THE POTENTIAL U(X).
      COMMON/DNUM/ZERO,ONE,TWO,THREE,FOUR
      COMMON/APARAM/C,D,RB,A,B
      COMMON/PARAM/Q,DL
      COMMON/UPARAM/CC(5,3,12),K(3,11),ZETA(3,11),IREAD
      COMMON/INDEXU/IU
```

```
      IF(IU.EQ.1) GO TO 12
      IU=1
      IF(IREAD.EQ.1) GO TO 10
      CALL READ
   12 IF(X.LE.RB) GO TO 10
      U=-TWO/X
      RETURN
   10 U=-(TWO/X)*(ONE+(Q-ONE)*(ONE-X/RB)**2/(ONE+C*X+D*X*X))
      RETURN
      END
C
C
C
      REAL FUNCTION GRAND(X,I)
C      THIS SUBROUTINE CALCULATES THE DIPOLE THNGTH INTEGRAND.
C      RC2P AND DRC2P ARE CORE WAVEFUNCTION AND ITS DERIVATIVE.
      DIMENSION RCO(200),RC2P(200)
      COMMON/UPARAM/C(5,3,12),K(3,11),ZETA(3,11),IREAD
      COMMON/WAVES/RCO,IGRAND,N,L
      COMMON/DNUM/ZERO,ONE,TWO,THREE,FOUR
      COMMON/GAM/GAMMA(11)
      COMMON/BNDWAV/RC2P
      COMMON/DCORE/DRC2P(200)
      IF(IGRAND.EQ.1) GO TO 9
      RC2P(I)=ZERO
      DRC2P(I)=ZERO
      LL=L+1
      LSIX=11-L
      DO 8 J=1,LSIX
      DPI=((TWO*ZETA(LL,J))**K(LL,J))*SQRT(TWO*
     1 ZETA(LL,J)/GAMMA(2*K(LL,J)+1))*X**K(LL,J)*
     1 EXP(-ZETA(LL,J)*X)*C(N,LL,J)
      RC2P(I)=RC2P(I)+DPI
      DRC2P(I)=DRC2P(I)+DPI*((FLOAT(K(LL,J))/X)-ZETA(LL,J))
    8 CONTINUE
    9 GRAND=RC2P(I)*RCO(I)*X
      RETURN
      END
C
C
C
      REAL FUNCTION GRANDV(X,I)
C      THIS SUBROUTINE CALCULATES THE DIPOLE VELOCITY INTEGRAND.
C      IT REQUIRES THE ARRAY DRC2P CALCULATED BY GRAND.
C     ***THIS FUNCTION SHOULD NOT BE CALLED BEFORE GRAND***
      DIMENSION RCO(200),RC2P(200)
      COMMON/BNDWAV/RC2P
      COMMON/DNUM/ZERO,ONE,TWO,THREE,FOUR
      COMMON/WAVES/RCO,IGRAND,N,L
      COMMON/DWAV/LM,LS
      COMMON/DCORE/DRC2P(200)
      SIGN=ONE
      IF(LS.EQ.LM) SIGN=-ONE
    9 GRANDV=RCO(I)*(SIGN*(TWO*FLOAT(L)+ONE+SIGN*ONE)
     1*RC2P(I)/(TWO*X)-DRC2P(I))
```

```
      RETURN
      END
C
C
C
      SUBROUTINE SIMPSN(STEP,RMAX,GRAND,VALUE)
C     INTEGRATION VIA SIMPSON'S RULE
C     FUNCTION TO BE INTEGRATED IS GRAND(X,I)
C     GRAND SHOULD BE DECLARED EXTERNAL
C     IMPLICIT REAL*8(A-H,O-Z)
      DATA ZERO,ONE,TWO,THREE,FOUR/0.E0,1.E0,2.E0,3.E0,4.E0/
      KOUNT=4
      VALUE=ZERO
      X=ZERO
      NMAX=RMAX/STEP
      DO 111 I=1,NMAX
      II=I
      X=X+STEP
      IF(KOUNT.EQ.4) GO TO 900
      KOUNT=4
      FT=TWO
      GO TO 901
  900 KOUNT=2
      FT=FOUR
  901 VALUE=VALUE+GRAND(X,II)*FT
  111 CONTINUE
      VALUE=VALUE*STEP/THREE
      RETURN
      END
C
C
C
      SUBROUTINE  PHASE(EN,LO,Q,NPTS,STEP,WAVM,DWAVM,WAVP,DWAVP,
     1DELTA,CLM,CLP,FM,FP,DFM,DFP,GM,GP,DGM,DGP)
C     PROGRAM TO CALCULATE DIFFERENCES IN PHASE SHIFTS
C      REQUIRES COULOMB FUNCTIONS WHICH MAY EITHER BE
C      CALCULATED BY SUBROUTINE COULMB OR READ FROM
C      FILE 24.
      COMMON/DNUM/ZERO,ONE,TWO,THREE,FOUR
      COMMON/PII/PI
      COMMON/PINDEX/IPHASE
      EK=SQRT(TWO*EN)
      ETA=-Q/EK
      RMATCH=FLOAT(NPTS)*STEP-STEP
      RHO=EK*RMATCH
      DLO=FLOAT(LO)
      DLM=FLOAT(LO-1)
      DLP=FLOAT(LO+1)
      IF(IPHASE.EQ.1) GO TO 55
      CALL COULMB(RHO,ETA,LO,FM,FO,FP,GM,GO,GP,SIGMA)
      WRITE(05,1) LO,EN,RHO,ETA,FO,FM,FP,GM,GO,GP
    1 FORMAT(I5,/9E12.4)
C     ***********************************************************
      IF(FO.GE.1.E020) GO TO 10
      WRITE(30,600) FM,FO,FP,GM,GO,GP,SIGMA
```

```
      GO TO 20
   10 READ(24,600) FM,FO,FP,GM,GO,GP,SIGMA
  600 FORMAT(8E14.7)
  601 FORMAT('ENERGY(HY)  ','  PHASE(LO-1)','   PHASE(LO+1)')
   20 CONTINUE
      DFP=(SQRT(DLP*DLP+ETA*ETA)*FO-(DLP*DLP/RHO+ETA)
     1 *FP)/DLP
      DGP=(SQRT(DLP*DLP+ETA*ETA)*GO-(DLP*DLP/RHO+ETA)
     1 *GP)/DLP
      DFM=((DLO*DLO/RHO+ETA)*FM-SQRT(DLO*DLO+ETA*ETA)*FO)/DLO
      DGM=((DLO*DLO/RHO+ETA)*GM-SQRT(DLO*DLO+ETA*ETA)*GO)/DLO
   55 CONTINUE
      ALP=(DWAVP*GP/EK)-WAVP*DGP
      BLP=WAVP*DFP-(DWAVP*FP/EK)
      ALM=(DWAVM*GM/EK)-WAVM*DGM
      BLM=WAVM*DFM-(DWAVM*FM/EK)
      CLP=SQRT(ALP*ALP+BLP*BLP)
      CLM=SQRT(ALM*ALM+BLM*BLM)
      SP=ZERO
      SM=ZERO
      SO=ZERO
      IF(BLP.LE.ZERO) SP=PI
      IF(BLM.LE.ZERO) SM=PI
      STEST=DLO*DLO+DLO-ETA**2
      IF(STEST.LE.ZERO) SO=PI
      DELTA=ATAN2(ETA*(TWO*DLO+ONE),(DLO*DLO+DLO-ETA**2))
     1+ATAN2(ALM,BLM)-ATAN2(ALP,BLP)+SP+SM+SO
C     ************************************
C     MODIFIED 10/14/76
      FASM=-ATAN2(ALM,BLM)
      FASP=-ATAN2(ALP,BLP)
      DELTA=FASP-FASM+ATAN2(ETA*(TWO*DLO+ONE),(DLO*DLO+DLO-ETA**2))
      KD=DELTA/(TWO*PI)
      KD=DELTA/PI-2*KD
      KD=DELTA/PI+KD
      DELTA=DELTA-FLOAT(KD)*PI
      WRITE(22,601)
C     ***************************************************
      WRITE(22,600) EN,FASM,FASP
C     *****************************************************
      RETURN
      END
C
C
C
      SUBROUTINE CSETUP(NPTS,WAVEB,WAVEC,R2EX,R2DIR,RTV,ENC,NDATA,
     1NSTEP,LO,NO,LC,NC,EO,ENSTEP,STEP,
     1EDATA,EDIFF,RDIRON,REXON,RTVON,CPOT)
C       THIS SUBROUTINE PARTIALLY CALCULATES THE DOUBLE INTEGRALS
C       NECESSARY TO INCLUDE CORRELATION EFFECTS.
C       SUBROUTINES USED:
C            BETAC      TO CALCULATE WAVEFUNCTIONS
C            READ       TO READ ORBITAL PARAMETERS
C            R2INT      TO PERFORM INTEGRATIONS
C
```

```
      DIMENSION WAVEB(NPTS),WAVEC(NPTS)
      DIMENSION EDATA(NDATA)
      DIMENSION ENC(40),CPOT(3)
      DIMENSION R2EX(NPTS,2,2,NSTEP),R2DIR(NPTS,2,NSTEP),RTV(2,NSTEP)
      DIMENSION RDIRON(NPTS,2,NDATA),REXON(NPTS,2,2,NDATA),
     1RTVON(2,NDATA)
      DIMENSION RINT(200),RDUM(200)
      DIMENSION DUM1(5),DUM2(5),DUM3(5)
      COMMON/SET/RCOM(200),RCOP(200),CLM,CLP
      COMMON/WAVES/RDUM,IGRAND,N,L
      COMMON/BNDWAV/RC2P(200)
      COMMON/APARAM/C,D,RB,A,B
      COMMON/DNUM/ZERO,ONE,TWO,THREE,FOUR
      COMMON/XSEC/ECORE
      EXTERNAL GRAND
C      ****************************************
      C=CPOT(1)
      D=CPOT(2)
      RB=CPOT(3)
      CALL READ
      N=NO
      L=LO
      DO 201 I=1,NPTS
      X=FLOAT(I)*STEP
      AA=GRAND(X,I)
      WAVEB(I)=RC2P(I)
  201 CONTINUE
      N=NC
      L=LC
      DO 15 I=1,NPTS
      X=FLOAT(I)*STEP
      AA=GRAND(X,I)
      WAVEC(I)=RC2P(I)
   15 CONTINUE
      IGRAND=1

      L1=IABS(LO-LC)
      L2=LO+LC
      IPSET=1
      ISET=0
      DO 10 NN=1,NSTEP
      ENC(NN)=EO+FLOAT(NN-1)*ENSTEP
      EN=ENC(NN)
      CALL BETAC(DUM1,DUM2,1,NPTS,EN,LC,NC,DUM3,DUM3,DUM3,
     1DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,
     2DUM3,DUM3,DUM3,DUM3,ISET,IPSET)
      IPSET=0
      CALL R2INT(NPTS,WAVEB,WAVEC,RCOM,RINT,RDUM,1,RDIP,ONE,ONE,
     1CLM,STEP)
      DO 20 I=1,NPTS
   20 R2DIR(I,1,NN)=RINT(I)
      RDV=DUM1(1)/(CLM*(EN-ECORE))
      RTV(1,NN)=(RDIP+RDV)/TWO
      CALL R2INT(NPTS,WAVEB,WAVEC,RCOP,RINT,RDUM,1,RDIP,ONE,ONE,
     1CLP,STEP)
```

```
      DO 30 I=1,NPTS
   30 R2DIR(I,2,NN)=RINT(I)
      RDV=DUM2(1)/(CLP*(EN-ECORE))
      RTV(2,NN)=(RDIP+RDV)/TWO
      IL=0
      DO 40 J=L1,L2,2
      IL=IL+1
      CALL R2INT(NPTS,RCOM,WAVEC,WAVEB,RINT,RDUM,J,RDIP,CLM,ONE,ONE,
     1STEP)
      DO 50 I=1,NPTS
   50 R2EX(I,1,IL,NN)=RINT(I)
      CALL R2INT(NPTS,RCOP,WAVEC,WAVEB,RINT,RDUM,J,RDIP,CLP,ONE,ONE,
     1STEP)
      DO 60 I=1,NPTS
   60 R2EX(I,2,IL,NN)=RINT(I)
   40 CONTINUE
   10 CONTINUE
      DO 100 NN=1,NDATA
      EN=EDATA(NN)+EDIFF
      IF(EN.LE.ZERO) GO TO 100
      CALL BETAC(DUM1,DUM2,1,NPTS,EN,LC,NC,DUM3,DUM3,DUM3,
     1DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,DUM3,
     2DUM3,DUM3,DUM3,DUM3,ISET,IPSET)
      CALL R2INT(NPTS,WAVEB,WAVEC,RCOM,RINT,RDUM,1,RDIP,ONE,ONE,
     1CLM,STEP)
      DO 200 I=1,NPTS
  200 RDIRON(I,1,NN)=RINT(I)
      RDV=DUM1(1)/(CLM*(EN-ECORE))
      RTVON(1,NN)=(RDIP+RDV)/TWO
      CALL R2INT(NPTS,WAVEB,WAVEC,RCOP,RINT,RDUM,1,RDIP,ONE,ONE,
     1CLP,STEP)
      DO 35 I=1,NPTS
   35 RDIRON(I,2,NN)=RINT(I)
      RDV=DUM2(1)/(CLP*(EN-ECORE))
      RTVON(2,NN)=(RDIP+RDV)/TWO
      IL=0
      DO 45 J=L1,L2,2
      IL=IL+1
      CALL R2INT(NPTS,RCOM,WAVEC,WAVEB,RINT,RDUM,J,RDIP,CLM,ONE,ONE,
     1STEP)
      DO 55 I=1,NPTS
   55 REXON(I,1,IL,NN)=RINT(I)
      CALL R2INT(NPTS,RCOP,WAVEC,WAVEB,RINT,RDUM,J,RDIP,CLP,ONE,ONE,
     1STEP)
      DO 65 I=1,NPTS
   65 REXON(I,2,IL,NN)=RINT(I)
   45 CONTINUE
  100 CONTINUE
      IGRAND=0
      RETURN
      END
C
C
C
      SUBROUTINE R2INT(NPTS,P1,P2,P3,RINT,RDUM,LPRM,RDIP,
```

```
     1CN1,CN2,CN3,STEP)
C        THIS SUBROUTINE PARTIALLY EVALUATES DOUBLE INTEGRALS
C    NEEDED BY SUBROUTINE CORR
      DIMENSION P1(NPTS),P2(NPTS),P3(NPTS),RINT(NPTS),RDUM(NPTS)
      COMMON/DNUM/ZERO,ONE,TWO,THREE,FOUR
      LPLUS=LPRM+1
      GRAND2=P2(1)*P3(1)
      GRAND3=P2(2)*P3(2)*FLOAT(2**LPRM)
      RINT(2)=FOUR*GRAND2+GRAND3
      RINT(1)=RINT(2)/TWO
C
      DO 10 J=4,NPTS,2
      GRAND1=GRAND3
      GRAND2=P2(J-1)*P3(J-1)*FLOAT((J-1)**LPRM)
      GRAND3=P2(J)*P3(J)*FLOAT(J**LPRM)
      RINT(J-1)=RINT(J-2)+(GRAND1+FOUR*GRAND2+GRAND3)/TWO
      RINT(J)=RINT(J-2)+(GRAND1+FOUR*GRAND2+GRAND3)
   10 CONTINUE
C
      RDIF=RINT(NPTS)*STEP**LPLUS/(CN2*CN3*THREE)
C
      GRAND4=P2(NPTS)*P3(NPTS)/FLOAT(NPTS**LPLUS)
      NJ-NPTS-1
      NJ1=NPTS-2
      GRAND5=P2(NJ)*P3(NJ)/FLOAT(NJ**LPLUS)
      GRAND6=P2(NJ1)*P3(NJ1)/FLOAT(NJ1**LPLUS)
      RDUM(NPTS)=ZERO
      RDUM(NJ1)=GRAND4+FOUR*GRAND5+GRAND6
      RDUM(NJ)=RDUM(NJ1)/TWO
      NMP=NPTS-2
C
      DO 20 J=4,NMP,2
      GRAND4=GRAND6
      NJ=NPTS-J
      NJ1=NJ+1
      GRAND5=P2(NJ1)*P3(NJ1)/FLOAT(NJ1**LPLUS)
      GRAND6=P2(NJ)*P3(NJ)/FLOAT(NJ**LPLUS)
      RDUM(NJ)=RDUM(NJ+2)+(GRAND4+FOUR*GRAND5+GRAND6)
      RDUM(NJ1)=RDUM(NJ+2)+(GRAND4+FOUR*GRAND5+GRAND6)/TWO
   20 CONTINUE
      GRAND4=GRAND6
      GRAND5=P2(1)*P3(1)
      RDUM(1)=RDUM(2)+(GRAND4+FOUR*GRAND5)/TWO
C
      CNSTNT=STEP/(CN1*CN2*CN3*9.0E00)
      K1=2
      DO 30 J=1,NPTS
      RINT(J)=P1(J)*((RINT(J)/FLOAT(J**LPLUS))+RDUM(J)*FLOAT
     1(J**LPRM))*FLOAT(2*K1)
      K1=(K1+1)/K1
      RINT(J)=RINT(J)*CNSTNT
   30 CONTINUE
      RETURN
      END
C
```

```
C
      REAL FUNCTION UMTRX(P4,RINT,NPTS,CN4)
      DIMENSION P4(NPTS),RINT(NPTS)
      VAL=0.0D0
      DO 10 J=1,NPTS
   10 VAL=VAL+P4(J)*RINT(J)
      VAL=VAL/CN4
      UMTRX=VAL
      RETURN
      END
C
C
C
      SUBROUTINE CORR(CORR1,CORR2,P4,CN4,NPTS,STEP,ENS,ENT,LQ,LV,LS,
     1EDIFF,II)
C     THIS SUBROUTINE CALCULATES INTERSHELL CORRELATION
C     CONTRIBUTIONS TO THE TRANSITION MATRIX ELEMENTS.
C       CORR1 IS THE REAL PART OF THIS CONTRIBUTION
C       CORR2 IS THE IMAGINARY PART OF THIS CONTRIBUTION.
C       FUNCTION SUBROUTINES USED ARE:
C                      UMTRX
C                      SIXJ
C                      D3J0
C       THIS SUBROUTINE ALSO USES ARRAYS CALCULATED BY CSETUP.
      DIMENSION P4(NPTS)
      DIMENSION ENC(40)
      DIMENSION RDIRON(200,2,40),REXON(200,2,2,40),RTVON(2,40)
      DIMENSION R2DIR(200,2,40),R2EX(200,2,2,40),RTV(2,40)
      COMMON/SETUP/ENC,RDIRON,REXON,RTVON,R2DIR,R2EX,RTV,NSTEP
      COMMON/DNUM/ZERO,ONE,TWO,THREE,FOUR
      COMMON/PII/PI
      CORSUM=ZERO
      CORD=ZERO
      COREX=ZERO
      DDIR=ZERO
      DEX=ZERO
      POLEA=ALOG(ABS(ENS-EDIFF-ENC(1)))
      POLEB=ALOG(ABS(ENS-EDIFF-ENC(NSTEP)))
      POLE=POLEA-POLEB
      LONE=IABS(LQ-LV)
      LTWO=LQ+LV
      XKS=SQRT(TWO*ENS)
      IF (ENT.LE.ZERO) GO TO 5
      XKT=SQRT(TWO*ENT)
    5 CONTINUE
      LTM=LV-1
      LTP=LV+1
      JI=0
      DO 30 LTT=LTM,LTP,2
C      CALCULATE FIRST THE DIRECT CONTRIBUTION.
      LT=LTT
      JI=JI+1
      DIRFAC=D3J0(LT,1,LV)
      DIRFAC=DIRFAC**2*TWO/THREE
      IF(ENT.LE.ZERO) GO TO 10
```

```
      DDIR=UMTRX(P4,RDIRON(1,JI,II),NPTS,CN4)
     1*(TWO/(PI*XKT))*RTVON(JI,II)
      CORS1=DDIR*DIRFAC
   10 CONTINUE
      CORD1=ZERO
      DO 15 KEN=1,NSTEP
      EN=ENC(NSTEP)
      DDIR2=UMTRX(P4,R2DIR(1,JI,KEN),NPTS,CN4)
     1*(TWO/(PI*SQRT(TWO*EN)))*RTV(JI,KEN)
   15 CORD1=CORD1+(DDIR2-DDIR)/(ENS-EN-EDIFF)
      CORD1=CORD1+DDIR*POLE
      CORD=CORD+FLOAT(2*LT+1)*CORD1*DIRFAC
      JEX=0
      DO 20 LPRMA=LONE,LTWO,2
      LPRM=LPRMA
      ITEST=(LS+LT-LPRM)*(LS-LT+LPRM)*(-LS+LT+LPRM)
      JEX=JEX+1
      IF(ITEST.GE.0) GO TO 40
      GO TO 20
   40 CONTINUE
      ISGN=LPRM+1+(LS+LQ+LV+LT)/2
      ISGN=ISGN-2*(ISGN/2)
      EXFAC=FLOAT((LS+LQ+2)*(LS+LQ)*(LV+LT+1))
      EXFAC=EXFAC/FLOAT((LV+LT+2)*(LV+LT)*(LS+LQ+1))
      EXFAC=SQRT(EXFAC)*D3JO(LS,LPRM,LT)*D3JO(LQ,LPRM,LV)*
     1SIXJ(1,LS,LQ,LPRM,LV,LT)*((-ONE)**ISGN)
      IF(ENT.LT.ZERO) GO TO 50
      DEX=UMTRX(P4,REXON(1,JI,JEX,II),NPTS,CN4)
     1*(TWO/(PI*XKT))*RTVON(JI,II)
      CORS1=CORS1+DEX*EXFAC
   50 CONTINUE
C
C       NOW CALCULATE THE EXCHANGE CONTRIBUTION.

      COREX1=ZERO
      DO 60 KEN=1,NSTEP
      EN=ENC(KEN)
      DEX2=UMTRX(P4,R2EX(1,JI,JEX,KEN),NPTS,CN4)
     1*RTV(JI,KEN)*(TWO/(PI*SQRT(TWO*EN)))
   60 COREX1=COREX1+(DEX2-DEX)/(ENS-EN-EDIFF)
      COREX1=COREX1+DEX*POLE
      COREX=COREX+COREX1*EXFAC*FLOAT(2*LT+1)
   20 CONTINUE
      CORS1=CORS1*FLOAT((2*LT+1)*(2*LV+1))
      CORSUM=CORSUM+CORS1
   30 CONTINUE
      CORR2=CORSUM
      CORR1=(CORD+COREX)*(ENC(2)-ENC(1))*FLOAT(2*LV+1)
      RETURN
      END
C
C
      REAL FUNCTION D3JO(L1,L2,L3)
C     THIS FUNCTION SUBROUTINE EVALUATES A 3-J SYMBOL
C     WITH LOWER ELEMENTS EQUAL TO ZERO.
```

```
      COMMON/GAM/GAMMA(11)
      IP=(L1+L2+L3)/2
      ITEST=L1+L2+L3-2*IP
      IF(ITEST.GE.1) GO TO 10
      DELTA=GAMMA(L1+L2-L3+1)*GAMMA(L1-L2+L3+1)
     1*GAMMA(-L1+L2+L3+1)/GAMMA(L1+L2+L3+2)
      D3J0=(-1.E0)**IP*SQRT(DELTA)*GAMMA(IP+1)/
     1(GAMMA(IP+1-L1)*GAMMA(IP+1-L2)*GAMMA(IP+1-L3))
      RETURN
   10 D3J0=0.E0
      RETURN
      END
C
C
C
      REAL FUNCTION SIXJ(L1,L2,L3,L4,L5,L6)
C      THIS FUNCTION SUBROUTINE EVALUATES A 6-J SYMBOL
C      WHICH HAS FIRST ELEMENT EQUAL TO ONE.
      IF(L1.NE.1) GO TO 10
      ITEST=IABS(L2-L3)
      IF(ITEST.GT.1)GO TO 70
      ITEST=IABS(L5-L6)
      IF(ITEST.GT.1) GO TO 70
      ITEST=(L4+L2-L6)*(L4-L2+L6)*(-L4+L2+L6)
      IF(ITEST.LT.0) GO TO 70
      ITEST=(L4+L3-L5)*(L4-L3+L5)*(-L4+L3+L5)
      IF(ITEST.LT.0) GO TO 70
      IA=2*L4
      IF(L5-L6) 20,30,40
   20 IC=2*L6
      IB=2*L2
      IF(L2-L3) 51,52,53
   30 IB=2*L6
      IC=2*L3
      IF(L2-L3) 52,54,60
   60 IC=2*L2
      GO TO 52
   40 IC=2*L5
      IB=2*L3
      IF(L3-L2) 51,52,53
   53 IS=(IA+IB+IC)/2
      SIXJ=FLOAT(IS*(IS+1)*(IS-IA)*(IS-IA-1))
     1/FLOAT((IB-1)*(IB)*(IB+1)*(IC-1)*(IC)*(IC+1))
      SIXJ=SQRT(SIXJ)*(-1.E0)**IS
      RETURN
   52 IS=(IA+IB+IC)/2
      SIXJ=FLOAT(2*IS*(IS-IA)*(IS-IB)*(IS-IC+1))
     1/FLOAT(IB*(IB+1)*(IB+2)*(IC-1)*(IC)*(IC+1))
      SIXJ=SQRT(SIXJ)*(-1.E0)**IS
      RETURN
   51 IS=(IA+IB+IC)/2
      SIXJ=FLOAT((IS-IB-1)*(IS-IB)*(IS-IC+1)*(IS-IC+2))
     1/FLOAT((IB+1)*(IB+2)*(IB+3)*(IC-1)*IC*(IC+1))
      SIXJ=SQRT(SIXJ)*(-1.E0)**IS
      RETURN
```

```
 54 IS=(IA+IB+IC)/2
    SIXJ=FLOAT(IB*(IB+1)*(IB+2)*(IC)*(IC+1)*(IC+2))
    SIXJ=FLOAT((IB*IB+2)+IC*(IC+2)-IA*(IA+2))*(-1.E0)**(IS+1)
   1/(2.E0*SQRT(SIXJ))
    RETURN
 70 SIXJ=0.E0
    RETURN
 10 WRITE(22,600) L1
600 FORMAT('*** USER INPUT NOT COMPATABLE...THIS SUBROUTINE'
   1,' VALID ONLY IF L1=1***',5X,'L1=',I3)
    STOP
    END
```

```
C          IF CORRELATIONS ARE NOT DESIRED, THE FLOLLOWING
C       SUBROUTINES ARE SUBSTITUTED FOR CSETUP AND CORR.
C
        SUBROUTINE CSETUP(A1,A2,A3,A4,A5,A6,A7,N1,N2,N3,N4,N5,N6,
       1B1,B2,B3,B4,B5,B6,B7,B8,B9)
        RETURN
        END
        SUBROUTINE CORR(C1,C2,A1,A2,N1,B1,B2,B3,N2,N3,N4,D1,I1)
        C1=0.00
        C2=0.00
        RETURN
        END
```

3. Subroutines for calculating Coulomb functions

```
      SUBROUTINE COULMB(SRHO,SETA,LO,FM,FO,FP,GM,GO,GP,SIG1)
C      THIS SUBROUTINE CALCULATES REGULAR (FL) AND IRREGULAR
C      (GL) COULOMB FUNCTIONS.
C            METHOD:  RECURSION RELATION METHOD OF STEGUN AND AB.
C       PHYS.REV. 98,1851 (1955) FOR RHO<8.0;  ASYMPTOTIC FORMULA
C       FOR RHO>8.0.
C      REQUIRES FUNCTION SUBROUTINE DIGAM.
      IMPLICIT REAL*8(A-H,O-Z)
      REAL SRHO,SETA,FM,FO,FP,GM,GO,GP,SIG1
C     GENERATOR OF REGULAR (F) AND IRREGULAR (G) COULOMB
C     FUNCTIONS
      REAL*8 II
      REAL*8 NINE
      DIMENSION FBAR(31),F(11),G(11),THETA(2),CGF(2),CL(2),
     1PL(2),QUPONP(2),CAPA(47),SMALLA(47)
      COMMON/DIGAMM/DIGAMX,DIGAMY
C     SET CONSTANTS
      DATA ACC/1.D-10/
      DATA ITOP/40/
      DATA PI/3.141592653589793D+00/
      DATA LTOP/8/
      DATA ZERO,ONE,TWO/0.D0,1.D0,2.D0/
      DATA THREE,FOUR,FIVE,SIX,SEVEN/3.D0,4.D0,5.D0,6.D0,7.D0/
      DATA EIGHT/8.D0/
      DATA NINE,TEN,ELEVEN,THRTEN/9.D0,10.D0,11.D0,13.D0/
      DATA EULER/0.5772156649014328 6D+00/
      DATA DTN6/1.D+05/
C     BNBN'S ARE BERNOULLI(2N)/2N.
      DATA BNBN2/    .833333333333333D-01 /
      DATA BNBN4/ -.833333333333333D-02 /
      DATA BNBN6/    .396825396825397D-02 /
      DATA BNBN8/ -.416666666666667D-02 /
      DATA BNBN10/    .757575757575757D-02 /
      DATA BNBN12/ -.210927960927961D-01 /
      DATA BNBN14/    .833333333333333D-01 /
      DATA BNBN16/ -.443259803921569D  00 /
      ETA=DBLE(SETA)
      RHO=DBLE(SRHO)
      IF(ETA.EQ.ZERO) GO TO 631
      ETASQ=ETA*ETA
      F1=ZERO
      F3=ZERO
      FO=ZERO
      PL(1)=TWO*ETA
      PL(2)=TWO*ETA*(ONE+ETASQ)/THREE
      LL=LTOP
      IASYM=0
      GO TO 1000
 1061 IF(RHO.GT.EIGHT) GO TO 1062
      COSQ=TWO*PI*ETA/(DEXP(TWO*PI*ETA)-ONE)
      CZERO=DSQRT(COSQ)
      CL(1)=CZERO
      CL(2)=DSQRT(ONE+ETASQ)*CZERO/THREE
      ZZZX=ONE
      ZZZY=ETA
```

```
      CALL DIGAM(ZZZX,ZZZY)
      RDIGAM=DIGAMX
      QUPONP(1)=-ONE+RDIGAM+TWO*EULER
      QUPONP(2)=(ONE/(FOUR*(ONE+ETASQ)))-(ELEVEN/SIX)+
     1RDIGAM+TWO*EULER
C     POWER SERIES COEFFICIENTS
      DO 18 L=0,1
      LPLUS=L+1
      CAPA(-L+3)=ZERO
      CAPA(-L-1+3)=ZERO
      CAPA(L+1+3)=ONE
      SMALLA(-L-1+3)=ZERO
      SMALLA(-L+3)=ONE
      SMALLA(L+1+3)=ZERO
      IMIN=-L+1+3
      IMAX=DABS(ETA)+ONE
      IF(IMAX.LT.8) IMAX=8
      RHOTOI=RHO**(-L)
      PSI=RHOTOI
   12 DO 11 I=IMIN,IMAX
      IF (I.EQ.L+1+3) GO TO 15
      CAPA(I)=(TWO*ETA*CAPA(I-1)-CAPA(I-2))/DFLOAT((I-3+L)*(I-3-L-1))
      SMALLA(I)=(TWO*ETA*SMALLA(I-1)-SMALLA(I-2)
     1-DFLOAT(2*(I-3)-1)*PL(LPLUS)*CAPA(I))/DFLOAT((I-3+L)*(I-3-L-1))
   15 RHOTOI=RHOTOI*RHO
      PSI=PSI+SMALLA(I)*RHOTOI
   11 CONTINUE
C     CHECK CONVERGENCE OF POWER SERIES
      TEST=DABS(SMALLA(IMAX)*RHOTOI/PSI)
      IF(TEST.LT.ACC) GO TO 14
      IF (IMAX.GT.ITOP) GO TO 6
      IMIN=IMAX+1
      IMAX=IMAX+5
      GO TO 12
    6 TYPE 600,ETA,RHO,L
  600 FORMAT(//,'ETA = 'D12.7,15X,'RHO = ',D12.7,15X,'L = ',I3)
      PRINT 333
      ILL=-L+3
      PRINT 444,(I,CAPA(I),SMALLA(I),I=ILL,IMAX)
  333 FORMAT(/,'POWER SERIES CONVERGENCE PROBLEMS',/5X,'I',
     19X,'CAPA(I)',28X,'SMALLA(I)')
  444 FORMAT(10X,I3,5X,2D28.13)
      STOP
   14 CONTINUE
      THETA(LPLUS)=PSI/(DFLOAT(L+L+1)*CL(LPLUS))
      CGF(LPLUS)=(TWO*ETA/COSQ)*(DLOG(TWO*RHO)+QUPONP(LPLUS))
  901 FORMAT(10X,I3,3(10X,D23.13))
   18 CONTINUE
C     CALCULATION OF FBAR(L) AS PER STEGUN AND AB.
C     PHYS. REV. 98,1851(1955)
   65 FBAR(LL+1+1)=ZERO
      FBAR(LL+1)=ONE
      DO 10 L=LL,1,-1
      LPLUS=L+1
      XL=DFLOAT(L)
```

```
      FBAR(LPLUS-1)=(TWO*XL+ONE)*(ETA+(XL*XL+XL)/RHO)*FBAR(LPLUS)
     1-XL*DSQRT((XL+ONE)**2+ETA**2)*FBAR(LPLUS+1)
      FBAR(LPLUS-1)=FBAR(LPLUS-1)/((XL+ONE)*DSQRT(XL*XL+ETA**2))
   10 CONTINUE
      IF(IASYM.EQ.1) GO TO 1002
C     USE WRONSKIAN RELATION TO SOLVE
C     QUADRATIC EQUATION FOR ALPHA
      AAA=FBAR(1)*FBAR(2)*(CGF(2)-CGF(1))
      BBB=FBAR(1)*THETA(2)-FBAR(2)*THETA(1)
      CCC=ONE/(ONE+ETASQ)
      CCC=-DSQRT(CCC)
      PM=-DSIGN(ONE,ETA)
      CHAR=BBB*BBB-FOUR*AAA*CCC
      IF(CHAR.LE.ZERO) GO TO 641
      DALBTH=FBAR(2)/DSQRT(BBB*BBB-FOUR*AAA*CCC)
      DALBT1=FBAR(1)/DSQRT(BBB*BBB-FOUR*AAA*CCC)
      IF(DALBTH.GT.1.D01) GO TO 638
      IF(DALBT1.GT.1.D01) GO TO 638
  639 CONTINUE
      ALPHA=(-BBB+PM*DSQRT(BBB**2-FOUR*AAA*CCC))/(TWO*AAA)
      GO TO 440
 1002 ALPHA=F(1)/FBAR(1)
C     NOTE, THIS IS 1/ALPHA IN NOTATION OF ST. AND AB.
  440 DO 44 L=1,6
      F(L)=FBAR(L)*ALPHA
   44 CONTINUE
      TEST0=((F0-F(1))/F(1))*DTN6
      TEST1=((F1-F(2))/F(2))*DTN6
      TEST3=((F3-F(4))/F(4))*DTN6
      IF(DABS(TEST0).GT.ONE) GO TO 45
      IF(DABS(TEST1).GT.ONE) GO TO 45
      IF(DABS(TEST3).GT.ONE) GO TO 45
      GO TO 47
   45 IF(LL.GT.25) GO TO 30
      F0=F(1)
      F1=F(2)
      F3=F(4)
      LL=LL+5
      GO TO 65
   47 IF(IASYM.EQ.1) GO TO 49
      G(1)=CGF(1)*F(1)+THETA(1)
   49 G(2)=(F(2)*G(1)+(ONE/DSQRT(ONE+ETASQ)))/F(1)
      DO 48 L=1,LO
      LPLUS=L+1
      DL=DFLOAT(L)
      G(LPLUS+1)=((TWO*DL+ONE)*(ETA+DL*(DL+ONE)/RHO)*G(LPLUS)-
     1(DL+ONE)*DSQRT(DL*DL+ETASQ)*G(LPLUS-1))/(DL*DSQRT(
     2(DL+ONE)**2+ETASQ))
   48 CONTINUE
   50 CONTINUE
      GM=SNGL(G(LO))
      GO=SNGL(G(LO+1))
      GP=SNGL(G(LO+2))
      FM=SNGL(F(LO))
      FO=SNGL(F(LO+1))
```

```
      FF=SNGL(F(LO+2))
      SIG1=SNGL(SIGMA)
      RETURN
  641 WRITE(05,642) CHAR,AAA,BBB,CCC,FBAR(1),FBAR(2)
  642 FORMAT('**** WARNING 641 ****',/,5X,'CHAR'
     1,12X,'AAA',12X,'BBB',12X,'CCC',12X,'FBAR(1)',
     2'FBAR(2)',/6D15.8)
      GO TO 45
C     ****************************************
C     ASYMPTOTIC SOLUTION FOR F(L) AND G(L)
C     ****************************************
 1000 CONTINUE
      IF(DABS(ETA).LT.1.5D0) GO TO 1050
      Y=DABS(ETA)
      SIGN=ETA/Y
      S=-ONE/(Y*Y)
      SIG=Y*DLOG(Y)-Y-PI/FOUR+Y*S*(BNBN2+S*(BNBN4/THREE+
     1S*(BNBN6/FIVE+S*(BNBN8/SEVEN+S*(BNBN10/NINE
     *+S*(BNBN12/ELEVEN+S*(BNBN14/THRTEN))
     2)))))
      SIGMA=SIGN*(SIG+PI/TWO)
      ERRSIG=BNBN16/(THREE*FIVE*Y**15)
 1060 CONTINUE
      LM=LO-1
      LP=LO+1
      IF(LO.EQ.1) GO TO 1068
      DO 1069 KK=1,LM
      DK=DFLOAT(KK)
 1069 SIGMA=SIGMA+DATAN((ETA/DK))
 1068 GO TO 1061
 1062 IASYM=1
      DO 1070 LLL=LM,LP
      TSTA=ONE
       DK=DFLOAT(LLL)
      CLLL=DFLOAT(LLL+1)
      CFIGX=ONE
      CFIGY=ZERO
      CPLUSX=ONE
      CPLUSY=ZERO
      DO 2 IN=1,30
      DN=DFLOAT(IN-1)
      DENOM=(DN+ONE)*TWO*RHO
      CPX=(CPLUSX*ETA*(ONE+TWO*DN)-CPLUSY*((DK-DN)*(DK+ONE+DN)
     1+ETA**2))/DENOM
      CPLUSY=(CPLUSY*ETA*(ONE+TWO*DN)+CPLUSX*((DK-DN)*(DK+ONE+DN)
     1+ETA**2))/DENOM
      CPLUSX=CPX
      TSTA1=CPLUSX**2+CPLUSY**2
      IF(TSTA.LT.TSTA1) GO TO 4
      TSTA=TSTA1
      CFIGX=CFIGX+CPLUSX
      CFIGY=CFIGY+CPLUSY
    2 CONTINUE
    4 CONTINUE
      FF=CFIGX
```

```
      GG=CFIGY
      THET=(RHO-ETA*DLOG(TWO*RHO)+SIGMA)-DFLOAT(LLL)*PI/TWO
      F(LLL+1)=GG*DCOS(THET)+FF*DSIN(THET)
      G(LLL+1)=FF*DCOS(THET)-GG*DSIN(THET)
      ERRFF=CPLUSX
      ERRGG=CPLUSY
      SIGMA=SIGMA+DATAN((ETA/CLLL))
 1070 CONTINUE
      LOP=LO+1
C     WRITE(05,1600) RHO,ETA,F(LOP),G(LOP),ERRFF,ERRGG,ERRSIG
      GO TO 50
 1600 FORMAT(/,'**** WARNING 1600 ****',/10X,'USING ',
     1'ASSYMPTOTIC FORMULA FOR ZERO ORDER COULOMB WAVES',
     2'---- ACCURACY IS SUSPECT'/10X,'RHO=',D18.10,
     35X,'ETA=',D18.10,5X,'FO=',D18.10,5X,'GO=',D18.10,
     4/5X,'FF ERROR=',D15.7,5X,'GG ERROR=',D15.7,
     55X,'SIGMA ERROR=',D15.5)
 1050 SIGMA=-EULER*ETA
      DO  3 I=1,50
      S=DFLOAT(I)
      SIGMA=SIGMA+ETA/S-DATAN((ETA/S))
    3 CONTINUE
      ERRSIG=ETA/S-DATAN((ETA/S))
       GO TO 1060
  638 WRITE(05,640) DALBTH,DALBT1
      TYPE 601,ETA,RHO
  601 FORMAT(//,'ETA = ',D12.7,'RHO = ',D12.7)
      GO TO 639
  640 FORMAT(//,'**** WARNING 640 ****'/10X,'DALBTH =',D13.7
     1,5X,'DALBT1 =',D13.7)
  631 CONTINUE
   30 TYPE 666,LL,RHO,ETA,FO,F(1),F1,F(2),F3,F(4)
      TYPE 602,DALBTH,DALBT1
  602 FORMAT(//,'DALBTH - ',D12.7,15X,'DALBT1 = ',D12.7)
  666 FORMAT(10X,'CONVERGENCE PROBLEMS WITH THE FOLLOWING ',
     1'SYMPTOMS',/5X,'LL=',I3,'      RHO=',D23.13,'      ETA=',D23.13,
     2/10X,'FO=',D23.13,'      F(0)=',D23.13,/10X,'F1=',
     3D23.13,'      F(1)=',D23.13,/10X,'F3=',D23.3,'F(3)=',
     4D23.13)
      TYPE 603,COSQ,CL,RDIGAM,QUPONP
  603 FORMAT(//,'COSQ - ',D12.7,10X,'CL = ',D12.7,10X,'RDIGAM = ',
     1D12.7,10X,'QUPONP - ',D12.7)
      TYPE 604,FBA,THETA,CGF,AAA,BBB,CCC,ALPHA
  604 FORMAT(//,'FBAR = ',D12.7,10X,'THETA = ',D12.7,10X,'CGF = ',
     1D12.7,/,'AAA = ',D12.7,10X,'BBB = ',D12.7,10X,'CCC = ',D12.7,
     110X,'ALPHA = ',D12.7)
      STOP
      END
C
C
C
C
      SUBROUTINE DIGAM(XZ,YZ)
C     DIGAMMA (PSI) FUNCTION. SEE A&S 6.3.
C     REQUIRES FUNCTION CDCOT(Z)..COMPLEX COTANGENT.
```

```
C       WRITTEN BY J. DOW (U. OF ILL.).
C       NOT TESTED YET ***********************
C        TESTED 3AUG72 FOR ABS(X,Y).LT.30.. ZZ=X+I*Y.
C        AGREES WITH A&S TABLES TO ACCURACY OF THOSE TABLES.
C       METHOD OF CALCULATION: USE ASYMPTOTIC FORMULA FOR X
C        BIG; PLUS RECURRENCE,REFLECTION,CONJUGATION.
        IMPLICIT REAL*8(A-H,O-Z)
        COMMON/DIGAMM/DIGAMX,DIGAMY
        COMMON/CDCOTN/COTX,COTY
        DATA HL2P/.918938533204673D+00/
        DATA HALF/.5D+00/
        DATA R40/40.D+00/
        DATA R50/50.D+00/
        DATA RFOURM/-4.D+00/
        DATA ONE/1.D+00/
        DATA RONE/1.D+00/
        DATA RTWO/2.D+00/
        DATA RZERO/0.D+00/
        DATA REPI/3.14159265358979D+00/
        DATA RPI/3.14159265358979D+00/
        DATA R2PI/6.28318530717959D+00/
        DATA RPIPE/3.1416D+00/
        DATA PI/3.14159265358979D+00/
        DATA TWOPI/6.28318530717959D+00/
        DATA ZERO/0.D+00/
        DATA R10/10.D+00/
        DATA R12/12.D+00/
        DATA RTNM9/.1D-08/
C       BNBN'S ARE BERNOULLI(2N/2N.
        DATA BNBN2/  .833333333333333D-01/
        DATA BNBN4/ -.833333333333333D-02/
        DATA BNBN6/  .396825396825397D-02/
        DATA BNBN8/ -.416666666666667D-02/
        DATA BNBN10/  .757575757575757D-02/
        DATA BNBN12/ -.210927960927961D-01/
        DATA BNBN14/  .833333333333333D-01/
        DATA BNBN16/ -.443259803921569D 00/
        DATA BNBN18/  .305395433027012D 01/
        DATA BNBN20/ -.264562121212121D 02/
        X=XZ
        Y=YZ
        PLUSX=ZERO
        PLUSY=ZERO
        RECURX=ZERO
        RECURY=ZERO
        ICSTAR=0
        ITHRU=0
        IF(X)32,32,3
      3 IF(Y)9,8,8
      8 IF(X.LT.R10) GO TO 5
C       EVALUATE DIGAMMA FROM ASYMPTOTIC SERIES FOR X.GT.10..
     88 ZINVX=X/(X**2+Y**2)
        ZINVY=-Y/(X**2+Y**2)
        XS=ZINVX**2-ZINVY**2
        YS=RTWO*ZINVX*ZINVY
```

```
      S=DSQRT(XS**2+YS**2)
      SPHS=DATAN2(YS,XS)
      DLOGZX=HALF*DLOG(X**2+Y**2)
      DLOGZY=DATAN2(Y,X)
      DIGAMX=DLOGZX-HALF*ZINVX-S*(BNBN2*DCOS(SPHS)+S*(BNBN4*DCOS
     1(2.D0*SPHS)+S*(BNBN6*DCOS(3.D0*SPHS)+S*(BNBN8*DCOS(4.D0*SPHS)
     2+S*(BNBN10*DCOS(5.D0*SPHS)+S*(BNBN12*DCOS(6.D0*SPHS)+S*
     3(BNBN14*DCOS(7.D0*SPHS)))))))+RECURX
      IF(X.LT.ZERO) DLOGZY=DSIGN(ONE,Y)*(PI-DABS(DLOGZY))
      DIGAMY=DLOGZY-HALF*ZINVY-S*(BNBN2*DSIN(SPHS)+S*(BNBN4*DSIN
     1(2.D0*SPHS)+S*(BNBN6*DSIN(3.D0*SPHS)+S*(BNBN8*DSIN(4.D0*SPHS)
     2+S*(BNBN10*DSIN(5.D0*SPHS)+S*(BNBN12*DSIN(6.D0*SPHS)+S*
     3(BNBN14*DSIN(7.D0*SPHS)))))))+RECURY
      IF(ICSTAR.EQ.1) DIGAMY=-DIGAMY
      DIGAMX=DIGAMX+PLUSX
      DIGAMY=DIGAMY+PLUSY
      RETURN
C
  314 PRINT 315,X,Y
  315 FORMAT(1X,'STOP315DIGAM.CANNOT REACH.DIGAM=',2D16.8)
      STOP
C
    9 ICSTAR=1
C     Y IS NEGATIVE
      Y=-Y
      GO TO 8
C
C
    5 IF(ITHRU)106,107,106
C     X BETWEEN 0.,10.. USE RECURRENCE.
  107 ITHRU=1
      N=R12-X
      IF(N)104,104,103
  103 DO 101 I=1,N
      RECURX=RECURX-X/(X**2+Y**2)
      RECURY=RECURY+Y/(X**2+Y**2)
  101 X=X+RONE
      GO TO 88
C
  104 PRINT 105,N,XZ,YX
  105 FORMAT(1X,'STOP105DIGAM.CANNOT REACH.N,ZZ=',I8,2D16.8)
      STOP
  106 PRINT 108,ITHRU,XZ,YZ
  108 FORMAT(1X,'STOP108DIGAM.CANNOT REACH.ITHRU,ZZ=',
     1    I8,2D16.8)
      STOP
C
    2 IF(X) 22,24,3
   22 IZZ=-X
C     CHECK POSSIBILITY OF ZZ EQUAL NON-POSITIVE INTEGER.
      RXX=IZZ
      RXXXX=RXX+X
      IF(DABS(RXXXX).GT.RTNM9*RXX) GO TO 6
   24 PRINT 23,XZZ,YZZ
   23 FORMAT(1X,'STOP23DIGAM.POLE AT ZZ=',2D16.8)
```

```
      STOP
C
   32 IF(Y)6,2,6
    6 ARGX=PI*X
      ARGY=PI*Y
C     NEGATIVE X. USE REFLECTION FORMULA.
      CALL CDCOT(ARGX,ARGY)
      PLUSX=-PI*COTX
      PLUSY=-PI*COTY
  703 X=RONE-X
      Y=-Y
      GO TO 3
C
      END
C
C
C
C
      SUBROUTINE CDCOT(X,Y)
C     COMPLEX COTANGENT FUNCTION.
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/CDCOTN/COTX,COTY
      DATA ZERO,ONE,TWO,THREE,FOUR/0.D+00,1.D+00,2.D+00,3.D+00,
     14.D+00/
      DATA RZERO/0.D+00/
      DATA TNM12/1.D-12/
      DATA TN18/18.D+00/
      IF(DABS(Y).GT.TN18) GO TO 19
      COTX=TWO*DSIN(TWO*X)*DEXP(TWO*Y)
      COTY=ONE-DEXP(FOUR*Y)
      BOT=ONE+DEXP(FOUR*Y)-TWO*DEXP(TWO*Y)*DCOS(TWO*X)
      RX=DABS(BOT)
      IF(RX.LT.TNM12) GO TO 12
   17 COTY=COTY/BOT
      COTX=COTX/BOT
      RETURN
C
C     DABS(Y).GT.18
   19 COTX=ZERO
      COTY=ONE
      IF(Y.LT.ZERO) COTY=-COTY
      RETURN
C
   12 PRINT 15,X,Y,RX
   15 FORMAT(1X,'WARNING15CDCOT.POLE AT Z=',2D12.5/,D13.5,
     1  '=SIN(Z).')
      GO TO 17
C
      END
```

REFERENCES

1. C. A. Swarts, D. L. Miller, and J. D. Dow, to be published.

2. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

3. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

4. J. C. Slater, Phys. Rev. 81, 385 (1951).

5. D. J. Kennedy and S. T. Manson, Phys. Rev. A5, 227 (1972).

6. M. Ya. Amusia, N. A. Cherepkov, and L. V. Chernysheva, Sov. Phys. JETP 33, 90 (1971); and Phys. Lett. 40A, 15 (1972).

7. M. Ya. Amusia and N. A. Cherepkov, Case Studies in Atomic Physics 5, 47 (1975).

8. M. Ya. Amusia, V. K. Ivanov, N. A. Cherepkov, and L. V. Chernysheva, Phys. Lett. 40A, 361 (1972).

9. M. Ya. Amusia, in Atomic Physics 5, eds. R. Marrus, M. Prior, and H. Shugart (Plenum Press, New York, 1977), p. 537.

10. D. L. Miller and J. D. Dow, Phys. Lett. 60A, 16 (1977).

11. Equation (1) may be genralized to account for partially or elliptically polarized light. See J. A. R. Samson, J. Opt. Soc. Am. 59, 356 (1969) and J. A. R. Samson and A. F. Starace, J. Phys. B 8, 1806 (1975).

12. J. Cooper and R. N. Zare, in Lectures in Theoretical Physics, Vol. XI-C, eds. S. Geltman, K. Mahanthappa, and W. Brittin (Gordon and Bireach New York, 1969), p. 317.

13. J. Cooper, Phys. Rev. 128, 681 (1962).

14. R. G. Houlgate, J. B. West, K. Codling, and G. V. Marr, J. Phys. B 7, L 470 (1974); and J. Elec. Spec. 9, 1205 (1976).

15. P. S. Bagus, T. L. Gilbert, and C. C. J. Roothaan, J. Chem. Phys. 56, 5195 (1972).

16. E. Clementi and C. Roetti, Atom. Data and Nucl. Data Tables 14, 177(1974).

17. J. M. Blatt, J. Comp. Phys. 1, 382 (1967).

18. The Padé Approximant in Theoretical Physics, eds. G. A. Baker and J. L. Gammel (Academic Press, New York, 1970).

19. J. L. Dehmer, W. A. Chupka, J. Berkowitz, and W. T. Jivery, Phys. Rev. A12, 1966 (1975).

20. W. S. Watson and D. T. Stewart, J. Phys. B7, L 466 (1974).

21. J. A. R. Samson, in: Advances in Atomic and Molecular Physics, Vol. 2, eds. D. R. Bates and I. Estermann (Academic Press, New York, 1966), p. 177.

22. P. G. Burke and K. T. Taylor, J. Phys. B 8, 2620 (1975).

23. J. A. R. Samson and J. L. Gardner, Phys. Rev. Lett. 33, 875 (1974).

24. L. Torop, J. Morton, and J. B. West, J. Phys. B 9, 2035 (1976).

25. D. L. Miller, J. D. Dow, R. G. Houlgate, G. V. Marr, and J. B. West, J. Phys. B 10, 3205 (1977).

26. G. V. Marr and J. B. West, Atom. Data and Nucl. Data Tables 18, 497 (1976).

27. S. T. Manson, Phys. Rev. 182, 97 (1969).

28. J. B. West, P. R. Woodruff, K. Codling, and R. G. Houlgate, J. Phys. B 9, 407 (1976).

29. M. J. Seaton, C. R. Acad. Sci., Paris 240, 1317 (1955).

30. C. E. Moore, Atomic Energy Levels NBS Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

31. A. Messiah, Quantum Mechanics, Vols. I and II, (John Wiley & Sons, New York, 1966).

32. K. Gottfried, Quantum Mechanics, Vol. K, (Benjamin, New York, 1966).

33. G. Breit and H. A. Bethe, Phys. Rev. 93, 888 (1954).

34. M. Rotenberg, R. Bivens, N. Metropolis, and J. K. Wooten, Jr., The 3-j and 6-j Symvols, (Technology Press, Cambridge, 1959).

CHAPTER THREE:

EXTENDED HÜCKEL THEORY OF THE NITROGEN TRAP IN GALLIUM ARSENIDE PHOSPHIDE

I. INTRODUCTION

In this chapter, we apply the extended Hückel theory to the nitrogen trap in $GaAs_{1-x}P_x$. This alloy, which has found use as a light emitting diode, possesses the desirable feature that the band gap ranges from the direct, infrared gap (1.5 ev) of GaAs to the indirect, green (2.2 eV) gap of GaP. Thus by controlling the composition x, one may select a desired color. With the implantation of N in amounts as small as $10^{17}/cm^3$ the luminescence is dominated by electron hole recombination from an impurity level located just below the conduction band edge ($\sim$.05 to $\sim$.2 eV).[1/] This level behaves as a deep trap,[2/] and as such is not amenable to the effective mass theory which is suitable for shallow donors and acceptors.[3/]

Extended Hückel theory is an extremely simple method for determining electronic energy levels and wavefunctions. Its principal applications have been in studies of large organic molecules[4/] and of deep impurity levels of covalent materials,[5-7/] where other methods are either unavailable or inappropriate. The method ultimately relies upon an attempt to guess the matrix elements, $\langle\phi_i|H|\phi_j\rangle$, of the Hartree-Fock operator between atomic orbitals ϕ_i. The wavefunctions are written as a linear combination of these atomic orbitals (LCAO) and a secular equation is solved to find the energy levels and wavefunctions. Attempts to justify, from first principles, the various prescriptions for estimating the Hamiltonian matrix elements have,

at best, met with limited success.[8/] To be honest, one must say that the real justification for use of extended Hückel theory is that it often works.

In spite of its shortcomings, extended Hückel theory does possess the following advantages: (i) Because it does not attempt a rigorous evaluation of matrix elements, it can be applied quickly and easily for a range of chemical compositions x. (ii) It is well suited for the inclusion of lattice deformations surrounding a defect, which we expect to be important in locating the N level within the band gap.

It seems worthwhile, then, to apply this method to the nitrogen trap. But, mindful of its limitations, one must interpret the results with caution.

II. METHOD

A. The Extended Hückel Hamiltonian

As was noted earlier, extended Hückel theory is an LCAO method in which one attempts to guess the matrix elements of the HF operator, H. A standard prescription[5/] gives

$$\langle\phi_i|H|\phi_j\rangle \quad H_{ij} = -(1/2)(I_i+I_j)\kappa_{ij}S_{ij} \tag{1}$$

where ϕ_i is an atomic orbital, I_i is the ionization potential of orbital ϕ_i, $S_{ij} = \langle\phi_i|\phi_j\rangle$ is the overlap of orbitals ϕ_i and ϕ_j, and κ_{ij} is a coupling constant. In normal applications we have

$$\kappa_{ij} = \kappa - (\kappa-1)\delta_{ij} \tag{2}$$

with $1 < \kappa < 2$ (δ_{ij} is the Kronecker delta). The overlap matrix, S, is formed by direct integration of the atomic orbitals.

Having formed the matrices S and H, one solves the secular equation

$$\sum_j (H_{ij}-E_kS_{ij})C_{jk} = 0 \tag{3}$$

to obtain eigenvalues E_k and corresponding eigenvectors $\psi_k = \sum_j C_{jk}\phi_j$.

B. Perfect Crystals

Since, in principle, the dimension of the secular equation is infinite, it is necessary to further simplify these equations. If one wishes to consider only perfect crystals,[9] one may form Bloch states

$$\phi_\ell(\vec{k},\vec{r}) = \sum_{\vec{R}_n} e^{i\vec{k}\cdot\vec{R}_n}\phi_\ell(\vec{r}-\vec{R}_n) \tag{4}$$

The secular equation then factors into a series of equations, one for each value of k in the Brillouin zone. The equations corresponding to (1) and (2) for this case are:

$$H_{ij}(\vec{k}) = \sum_n e^{i\vec{k}\cdot\vec{R}_n} H_{ij}^{\vec{R}_n}, \tag{5}$$

and

$$\sum_j [H_{ij}(\vec{k})-E_m(\vec{k})S_{ij}(\vec{k})]C_{jm}(\vec{k}) = 0, \tag{6}$$

where

$$H_{ij}^{\vec{R}_n} = -\frac{1}{2}\kappa_n(I_i+I_j)S_{ij}^{\vec{R}_n}, \tag{7}$$

$$S_{ij}^{\vec{R}_n} = \langle\phi_i(\vec{r})|\phi_j(\vec{r}-\vec{R}_n)\rangle, \tag{8}$$

and

$$S_{ij}(\vec{k}) = \sum_n e^{i\vec{k}\cdot\vec{R}_n} S_{ij}^{\vec{R}_n}. \tag{9}$$

If κ_{ij} is defined as in equation (2), then

$$\begin{aligned} \kappa_n &= 1 \quad \text{if} \quad \vec{R}_n = 0 \\ &= 0 \quad \text{otherwise.} \end{aligned} \tag{10}$$

Since one is usually interested only in the region near the band gap, equation (5) is further reduced by including only the valence orbitals of the free atoms.

C. Cluster Model

For the defect problem, Bloch's theorem is no longer applicable. In this case, one reduces the dimensions of equation (2) by selecting a cluster of atoms which includes the defect. Obviously, if the cluster is chosen large enough it will exhibit the properties of the infinite solid. On the other hand, this approach yields discrete levels, and for small clusters it is difficult to define the band edges precisely. This becomes especially important when the defect level lies close to the band edge. The level spacings within the band must be much smaller than the binding energy of the defect level for meaningful results.

In addition, surface effects become much more important as cluster size is decreased. Thus one must strike a balance between the desire to simulate an infinite crystal and the necessity of keeping the calculation tractable.

D. Periodic Impurities

A third type of calculation is actually a combination of perfect crystal and cluster calculations. Periodic boundary conditions may be applied to a cluster containing a defect, and equations (5)-(10) applied to this expanded basis. This represents extended Hückel theory as applied to a crystal with a periodic array or "superlattice" of impurities. For this approach to be successful, the unit cluster must be chosen large enough so that the dispersion of the impurity band is small compared to the band gap. This has proved to be a problem in previous applications.[6,10]

III. CALCULATIONS

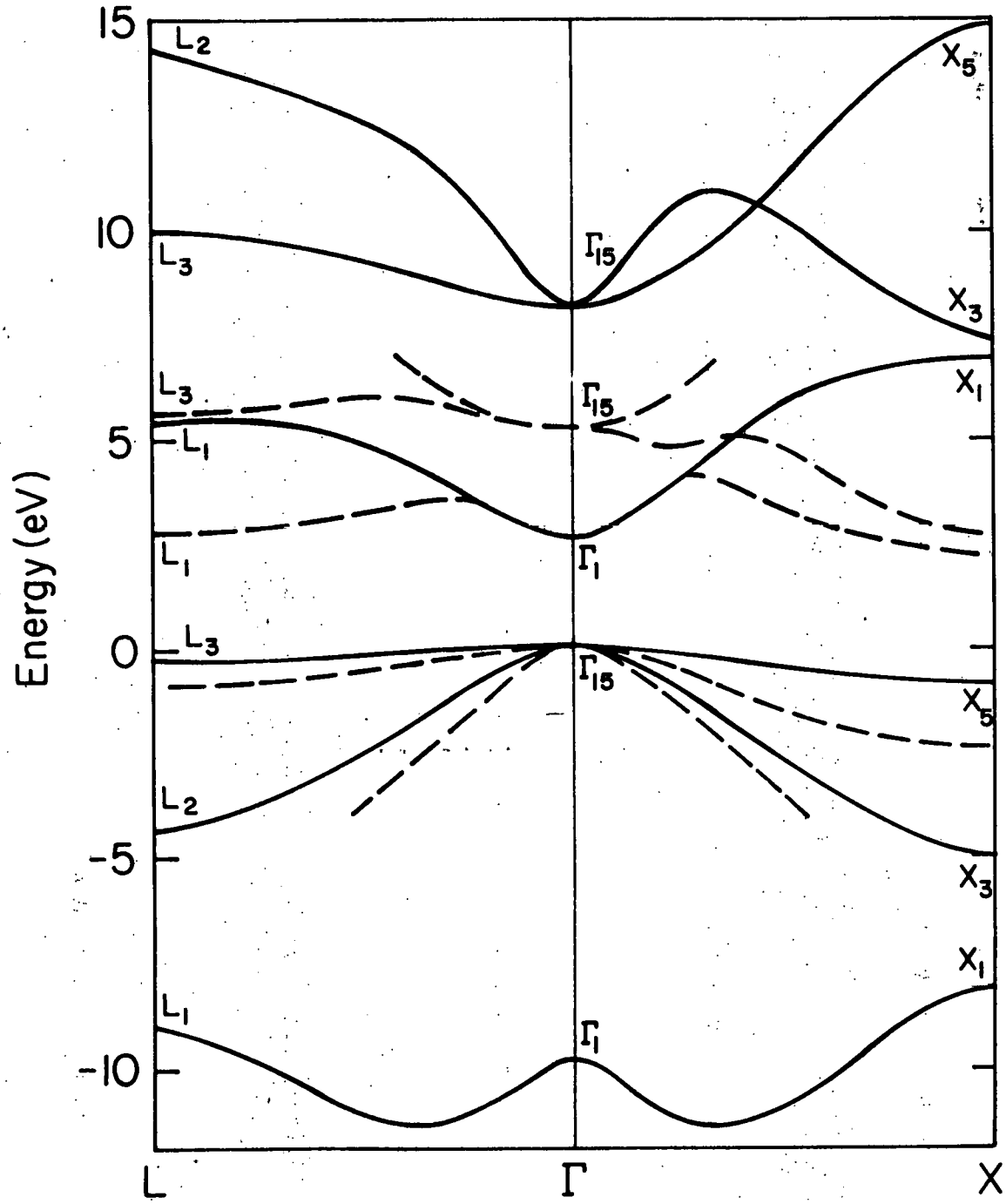
A. Band Structures

Before addressing the problem of the N-trap we have first calculated band structures for the perfect crystals in the binary limits, i.e., $x = 0$ and $x = 1$, using equations (5)-(10). The zincblende structure is an FCC lattice with two atoms per unit cell. We therefore start with a basis set of eight Bloch functions, corresponding to one s and three p functions for each atom in the unit cell, and must solve an eight by eight matrix equation for each k-point.

The necessary atomic wavefunctions were taken from the Roothaan-Hartree-Fock calculations of Clementi and Roetti.[11] Ionization potentials were taken from the tables of Moore,[12] and κ_n was treated as an adjustable parameter. The sums in equations (5) and (9) were carried out to eight nearest neighbors (two FCC lattice constants), which is quite sufficient for convergence.

For the first calculation the coupling constant was chosen as in equation (10), and κ was adjusted to bring the band gap at Γ ($\vec{k} = 0$) into agreement with the pseudopotential calculation of Cohen and Bergstresser.[13] We show in Figure 1 the resulting band structure ($\kappa = 1.26$) and compare it with the pseudopotential result. (The zero of energy has been shifted to coincide with Γ_{15}.) The valence bands produced here are in reasonable agreement with the pseudopotential result. The conduction bands, however, are poorly represented.

Fig. 1. Band structure of GaP: solid lines-extended Hückel with $\kappa = 1.26$, dashed lines-pseudopotential calculation of reference 13.


15
10
5
0
-5
-10
Energy (eV)
L
Γ
X
L2
L3
L3
L1
L1
L3
L2
L1
Γ15
Γ15
Γ1
Γ15
Γ1
X5
X3
X1
X5
X3
X1

As was pointed out by Messmer,[9] the X_1 point, which is of major importance here, may be lowered by reducing the strength of the s-p interaction. We therefore introduce a second coupling constant, κ', which is used for s-p matrix elements. With this modification we obtained the band structure shown in Figure 2. ($\kappa = 1.26$, $\kappa' = 1.11$). The agreement in this case is improved significantly. A similar analysis was carried out for GaAs, and the results are shown in Figure 3, ($\kappa = 1.47$, $\kappa' = 1.37$).

The results obtained here are not in close agreement with the pseudopotential calculations, particularly in the uppermost conduction bands of GaP, where reduction of the s-p interaction pulls L_2 below L_3. In spite of this, we felt that in view of the approximations of the model, these results warranted application of extended Hückel theory to $GaAs_{1-x}P_x$: N.

B. Cluster Calculations

We now turn our attention to the cluster calculations which treat the defect. The results presented here were obtained by using a 35-atom cluster consisting of all atoms not more than one (FCC) lattice constant distant from a central atom. Messmer and Watkins[5] have concluded that a cluster of this size is suitable for the study of defects in diamond.

Basis functions used included N 2s and 2p, Ga 4s and 4p, As 4s and 4p, and P 3s and 3p orbitals. All

Fig. 2. Band structure of GaP: solid lines-extended Hückel with $\kappa_{ss} = \kappa_{pp} = 1.26$, $\kappa_{sp} = 1.11$; dashed lines-pseudopotential calculation of reference 13.

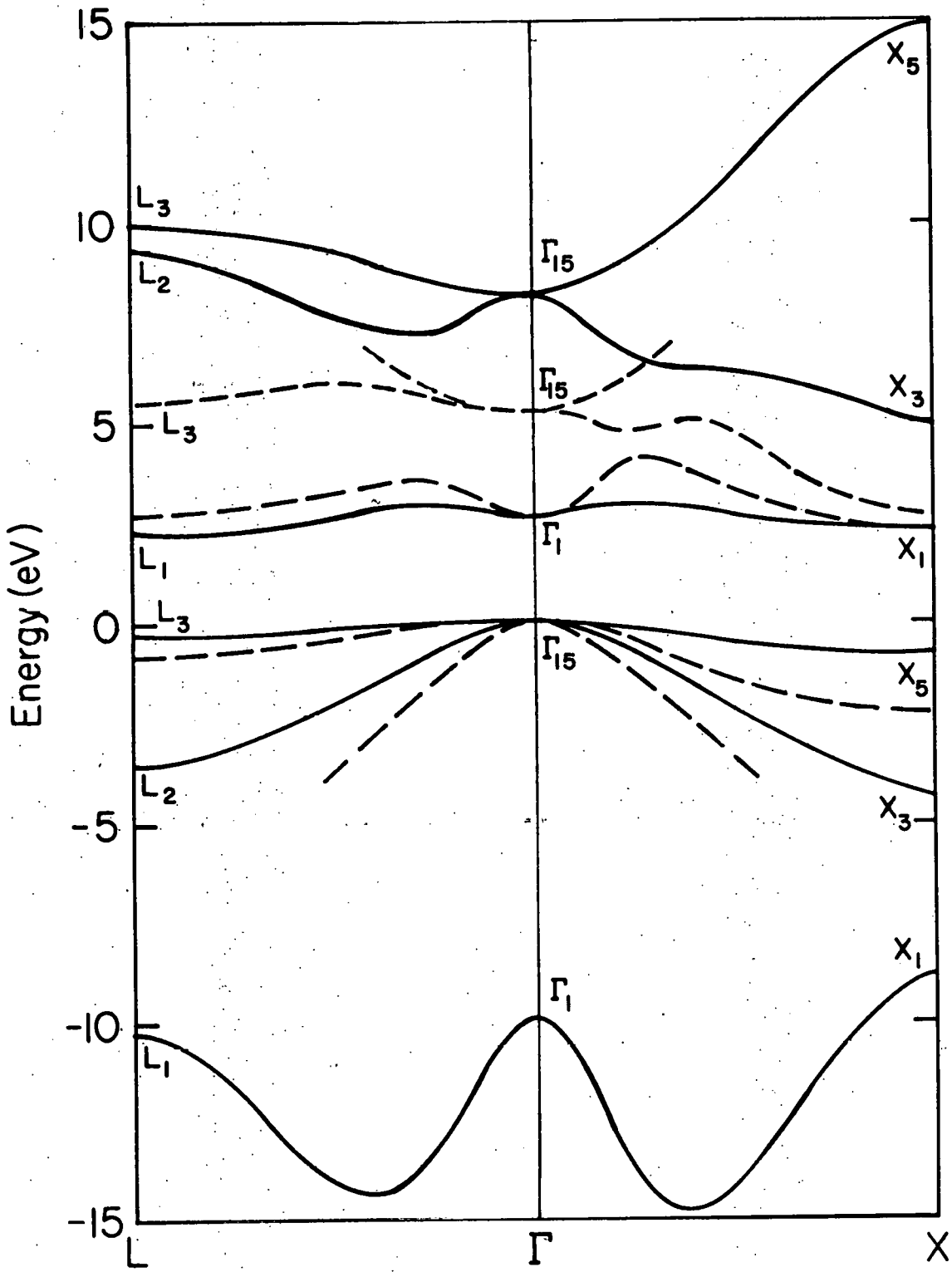
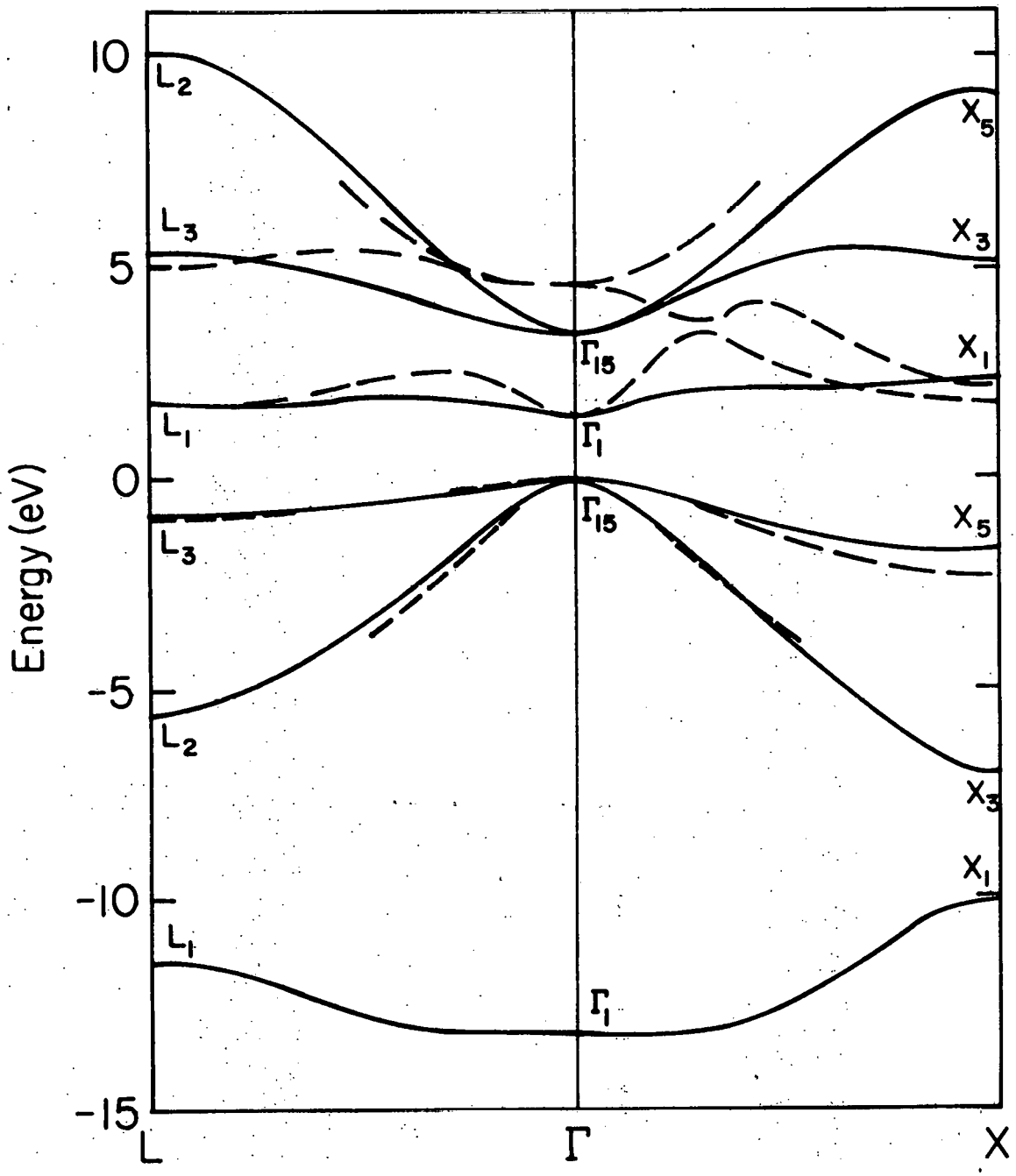

15
10
5
0
-5
-10
-15
Energy (eV)
L
Γ
X
L_3
L_2
L_3
L_1
L_3
L_2
L_1
Γ_{15}
Γ_{15}
Γ_1
Γ_{15}
Γ_1
X_5
X_3
X_1
X_5
X_3
X_1

Fig. 3. Band structure of GaAs: solid lines-extended Hückel with $\kappa_{ss} = \kappa_{pp} = 1.47$, $\kappa_{sp} = 1.37$; dashed lines-pseudopotential calculation of reference 13.


10
5
0
-5
-10
-15
Energy (eV)
L
Γ
X
L_2
L_3
L_1
L_3
L_2
L_1
Γ_{15}
Γ_1
Γ_{15}
Γ_1
X_5
X_3
X_1
X_5
X_3
X_1

were taken from reference 11. Charge dependent ionization potentials were obtained by linear interpolation:

$$I_i = I_i^0 + |q_i|(I_i^{\pm} - I_i^0) \tag{11}$$

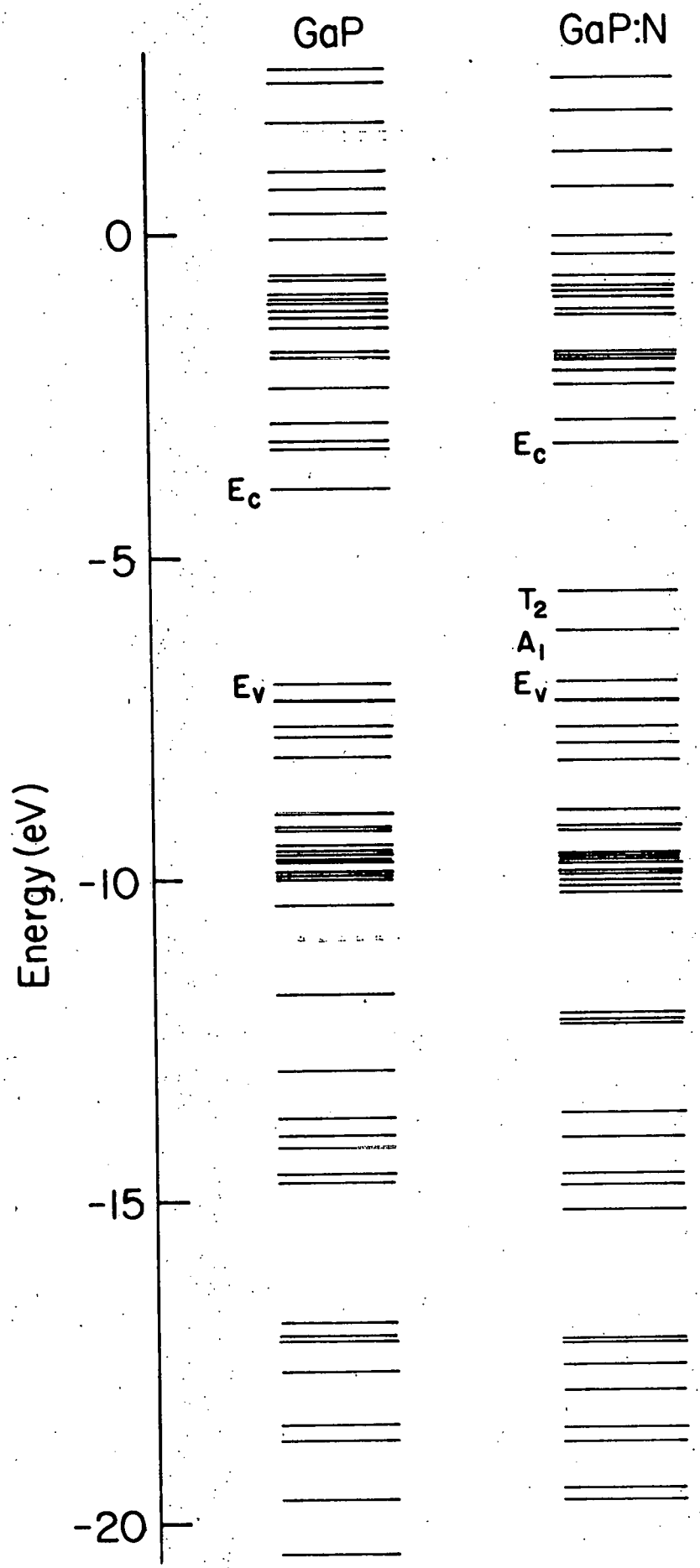
where I_i^0 is appropriate for the neutral atom, $I_i^{\pm}$ is the ionization potential for the positive (negative) ion, and q_i is the charge on the ion as determined by a Mulliken[14/] population analysis of the eigenfunctions (see Appendix A). This prescription necessitates an iterative solution since the q_i and I_i are interrelated. Note that the zeroth iteration corresponds to neutral atom potentials, which were used in the band structure calculations.

By taking advantage of the symmetry (T_d) of the cluster (see Appendix B) we were able to factor the secular equation so that the largest matrix involved was 22×22. Matrices of this size were easily handled numerically.

A number of calculations were performed, using different values of the parameter κ_{ij}. All yielded similar results. Typical results are shown in Figure 4, where we plot energy levels both for a GaP cluster and for a cluster with the central P atom replaced by an N atom. For this calculation we used a single coupling constant, $\kappa_{ij} = \kappa - (\kappa-1)\delta_{ij}$, with $\kappa = 1.25$. This gives a band gap in close agreement with the perfect crystal value.

We see from Figure 4 that the nitrogen impurity introduces two states in the gap, the lower state being of A_1 symmetry

Fig. 4. Extended Hückel levels of a 35-atom GaP cluster and the same cluster with N impurity on central site. E_c and E_v denote condution and valence band edges.


GaP
GaP:N
0
-5
-10
-15
-20
Energy (eV)
E_c
E_v
E_c
T_2
A_1
E_v

and the upper state possessing T_2 symmetry. Current experiments show only one impurity level (the A_1 state) within the gap of GaP and this level is much closer to the conduction band edge ($E_N \geq E_C - .2eV$) than either calculated level ($E_N \leq E_C - 1.5$ eV). This is a serious shortcoming of the present calculations. Attempts to improve this result by adjusting the input parameters (using ionic wavefunctions instead of atomic ones, adjusting the coupling constants, using multiple coupling constants, etc) were unsuccessful.

Even more disturbing is that almost identical results are obtained for GaAs, where experiment indicates that the impurity levels have been pushed out of the gap and into the conduction band. We comment further on these results below.

IV. CONCLUSIONS

A common concern about extended Hückel calculations is that they fail to take into account spatial variations in charge density, and should therefore be used only for covalent materials. In the band structure calculations presented here, such considerations were simply ignored and were not found to cause serious difficulties. One might therefore expect extended Hückel theory to provide useful information about the nitrogen impurity levels.

The cluster calculations carried out here have located the impurity states much too deep in the gap, and cannot be considered to successfully describe the nitrogen trap. We were, however, able to draw the following conclusions:

(i) For the GaP cluster, the two states at the bottom of the conduction band contain significant contributions from the central atom. These are the only states near the band edge which do. This happenstance appears to be an artifact of the manner in which we have selected our cluster. Given this and the strength of the nitrogen ionization potentials (∿40% larger than the P ionization potentials) it is not surprising that these states are pulled far into the gap by the nitrogen impurity. For any cluster calculations to be successful, the atomic orbitals of the central atom must be divided among many states near the conduction band edge.

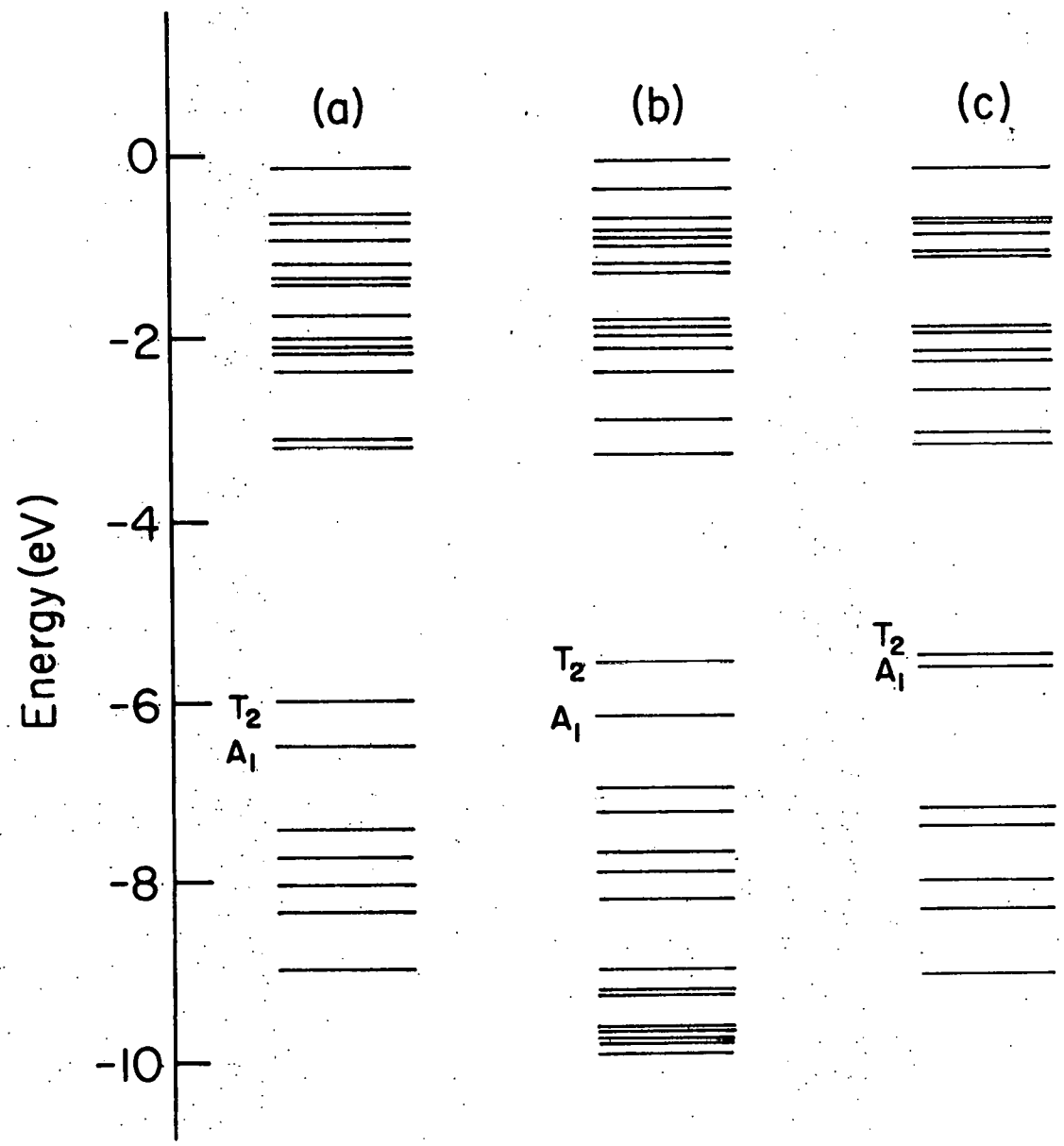
(ii) We do not view the presence of the T_2 state within the gap to be a serious difficulty. This state comes from the second conduction band $(\Gamma_{15} - X_3)$, which the Hückel

theory cluster model places at too low an energy; and in a more realistic calculation it is unlikely that the T_2 state would be drawn into the gap. Such a state should exist as a resonance, but would not have been observed in photoluminescence experiments.

(iii) Inward relaxation of the four Ga atoms adjacent to the impurity drives the impurity states deeper into the gap. Outward relaxation tends to raise these levels. This is illustrated in Fig. 5 where we display energy levels for the unrelaxed lattice, for the lattice with the neighboring Ga's relaxed outward by 10%, and for an inward relaxation of 5%. The situation here is reminiscent of the N impurity of diamond, where it has been shown[5/] that a large Jahn-Teller distortion may be responsible for lowering the impurity level. In view of these results, it is essential that an adequate treatment of the N-trap include lattice distortions.

In summary, we suggest that the failure of the cluster calculations to predict the binding energy of the N-trap is not due to the ionicity of GaAs and GaP, rather, it is due to a combination of the cluster approximation and the large size mismatch of the substitutional N and the host anion (P or As). The present choice of cluster singles out the two states at the bottom of the conduction band as being strongly associated with the eventual impurity site. These two states are then easily drawn into the gap by an N impurity which has a radius of ∿50% of the P radius, and ionization potentials ∿40% larger than those of P.

Fig. 5. Extended Hückel energy levels of 35-atom GaP:N cluster: (a) with four nearest neighbor Ga atoms relaxed inward 5%, (b) undistorted cluster, (c) with nearest-neighbor Ga's relaxed outward 10%.


(a)
(b)
(c)
0
-2
-4
-6
-8
-10
Energy (eV)
T_2
A_1
T_2
A_1
T_2
A_1

In a superlattice calculation, all anion sites are explicitly equivalent, and the perfect crystal case reproduces the band structure of Fig. 2. This would alleviate much of the difficulty encountered by the cluster calculations. We hesitate to recommend such an approach in view of previous applications[6,10] of this technique, which have been frustrated by the computational limitations of selecting a large enough cluster to reduce dispersion in the impurity bands to acceptable levels.

APPENDIX A

MULLIKEN POPULATION ANALYSIS

In this appendix we describe the Mulliken population analysis, which is used to assign charge to the ions in the extended Hückel cluster calculations.

Consider first a molecular orbital (MO), ψ, of a binary molecule which may be written

$$\psi = a_1\phi_1 + a_2\phi_2 \tag{1}$$

where ϕ_1 and ϕ_2 are atomic orbitals (AO's) centered on atoms 1 and 2 respectively. Assuming this MO is singly occupied, we wish to divide this charge between the two centers. We do this in the following way. The charge density is given by the square of the wavefunction

$$\psi^2 = a_1^2\phi_1^2 + 2a_1a_2S_{12}(\phi_1\phi_2/S_{12}) + a_2^2\phi_2^2 \tag{2}$$

where $S_{12} = \langle\phi_1|\phi_2\rangle$ is the overlap of orbitals ϕ_1 and ϕ_2. Upon integration over all space this becomes

$$1 = a_1^2 + 2a_1a_2S_{12} + a_2^2 \ . \tag{3}$$

Thus the charge is divided into three terms. The first of these should clearly be assigned to atom 1 and the last to atom 2. We are then left with an overlap population which we divide equally between the two sites. We then have

$$q_1 = -(a_1^2 + a_1 a_2 S_{12})$$
$$q_2 = -(a_2^2 + a_1 a_2 S_{12}) \tag{4}$$

for the charge on atoms 1 and 2 due to an electron in the MO ψ.

For the general case the MO is written

$$\psi_i = \sum_{r_k} a_{ir_k} \phi_{r_k} \tag{5}$$

where ϕ_{r_k} is the r-th orbital on atom k. We then have, analogously to equation (3),

$$1 = \sum_{r_k} [a_{ir_k}^2 + 2 \sum_{s_m \neq r_k} a_{ir_k} a_{is_m} S_{r_k s_m}]. \tag{6}$$

As above, the first term within the brackets is clearly associated with atom k, while terms of the second sum should be divided between atoms k and s. Thus we assign

$$q_k = -N(i) \sum_{i,r} [a_{ir_k}^2 + \sum_{s_m \neq r_k} a_{ir_k} a_{is_m} S_{r_k s_m}] \tag{7}$$

where N(i) is the occupation number of the i-th MO, and q_k is the total MO electronic charge on atom k. Note that in order to find the total charge of an atom one must include the nuclear charge and any core electrons which have been neglected in constructing the MO's.

While in most solids the concept of the charge on an atomic site is rather nebulous, the above discussion does provide a unique prescription for allocating the total charge among these sites.

APPENDIX B

CONSTRUCTION OF SYMMETRY ORBITALS

We demonstrate here how one may utilize the symmetry of a cluster to factor the secular equation of extended Hückel theory. The notation we use here is that of reference 15, to which we refer the reader for group theory details which are not presented here. We also describe group operations and list a set of irredicible representations of the tetrahedral point group (T_d).

1. Method

The projection operator corresponding to the k-th row and column of the j-th irredicible representation is given by

$$P^j_{KK} = \frac{\ell_j}{h} \sum_R \Gamma^j(R)_{KK} R$$

where ℓ_j is the dimension of the representation, h is the dimension of the point group, and $\Gamma^j(R)$ is the element of the representation corresponding to the group operation R.

If we define functions

$$F^j_K = P^j_{KK} f$$

and

$$G^i_\lambda = P^i_{\lambda\lambda} g$$

where f and g are arbitrary functions, a well known result of group theory is that

$$\langle G^i_\lambda | F^j_\kappa \rangle = 0 \quad \text{if } i \neq j \text{ or } \lambda \neq \kappa. \tag{1}$$

Or, in the jargon of group theory, functions belonging to different irredicible representations (i,j) or to different rows (κ,λ) of the same irredicible representation are orthogonal.

We apply this result as follows. First, we select a basis function ϕ_1. For the extended Hückel calculations, this would be an atomic orbital. We then apply the operations of the point group to obtain a set of functions $S_1 = \{R\phi_1\}$. Designate by n_1 the number of distinct functions in this set. We then apply the projection operators of the point group to elements of this set until n_1 linearly independent symmetry orbitals are found. These are necessarily linear combinations of elements of S_1. We then select a second orbital, (not in S_1) and apply the same procedure to this orbital. This process is repeated until the symmetry orbitals, or, equivalently, the sets S_i, span the original space of atomic orbitals.

The symmetry orbitals are then grouped according to representation and row and normalized according to $\sum_j a^2_{jk} = 1$, where a_{jk} is defined by

$$\psi_k = \sum_j a_{jk}\phi_j, \tag{2}$$

with ψ_k the k-th symmetry orbital. Finally, the unitary transformations aHa^{-1} and aSa^{-1}, where H and S are extended Hückel Hamiltonian and overlap matrices, reduce the secular equation (equation (3) of Chapter Three) to block form.

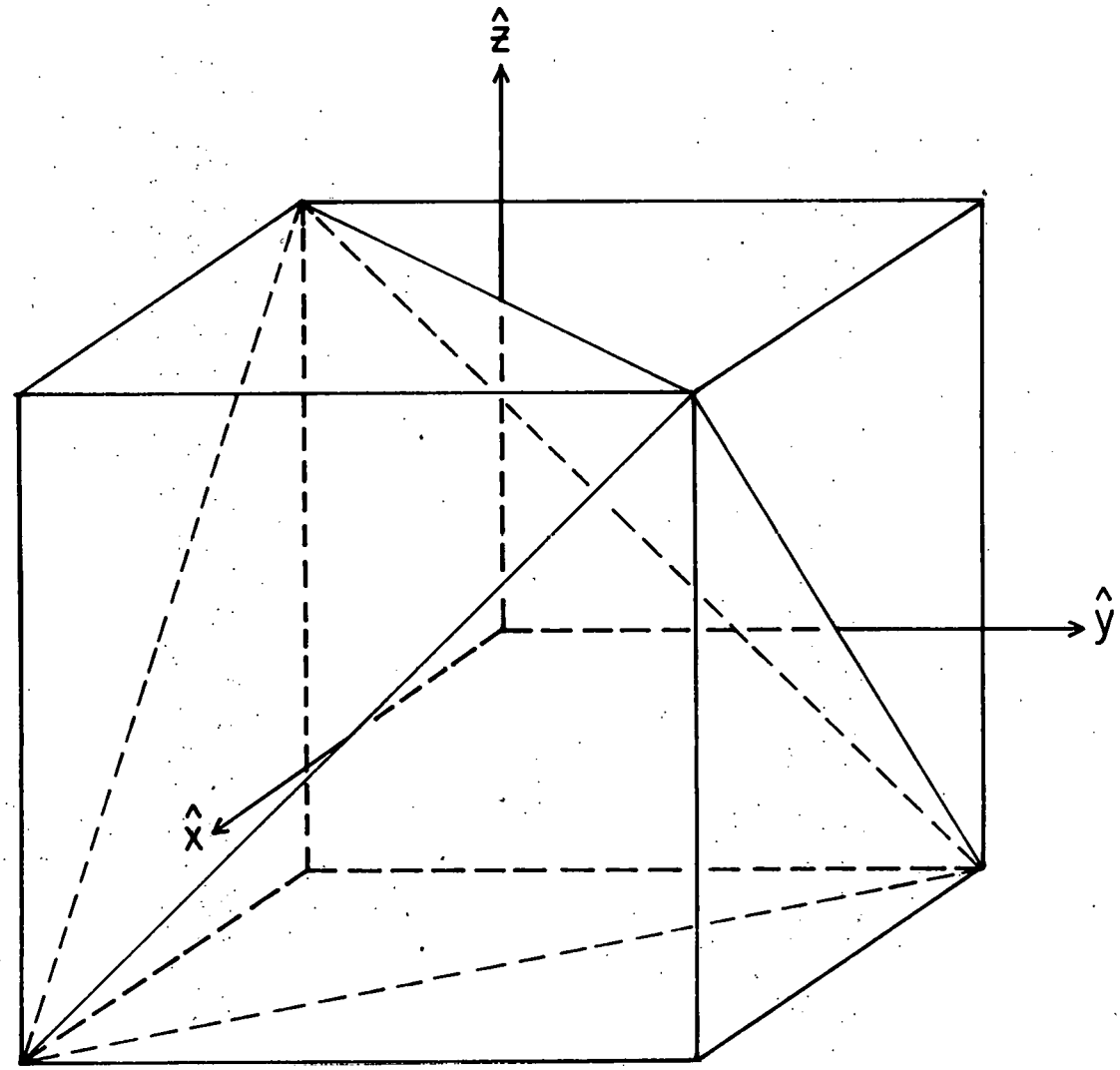
2. Irreducible Representations of T_d

a. Group Elements

We use as a guide the tetrahedron and coordinate system shown in Fig. 1. We can then describe the group elements as (active) rotations of the tetrahedron.

1. Identity
2. Rotation by π about x-axis
3. Rotation by π about y-axis
4. Rotation by π about z-axis
5. Rotation by $2\pi/3$ about (1,1,1)-axis
6. Rotation by $4\pi/3$ about (1,1,1)-axis
7. Rotation by $2\pi/3$ about (-1,-1,1)-axis
8. Rotation by $4\pi/3$ about (-1,-1,1)-axis
9. Rotation by $2\pi/3$ about (-1,1,-1)-axis
10. Rotation by $4\pi/3$ about (-1,1,-1)-axis
11. Rotation by $2\pi/3$ about (1,-1,-1)-axis
12. Rotation by $4\pi/3$ about (1,-1,-1)-axis
13. Reflection through $x-y = 0$ plane
14. Reflection through $x+y = 0$ plane
15. Reflection through $z-x = 0$ plane
16. Reflection through $z+x = 0$ plane

Fig. 1. Tetrahedron to illustrate group operations of T_d.


$\hat{z}$
$\hat{y}$
$\hat{x}$

17. Reflection through $z-y = 0$ plane
18. Reflection through $z+y = 0$ plane
19. Rotation of $\pi/2$ about z-axis followed by inversion
20. Rotation of $-\pi/2$ about z-axis followed by inversion
21. Rotation of $\pi/2$ about y-axis followed by inversion
22. Rotation of $-\pi/2$ about y-axis followed by inversion
23. Rotation of $\pi/2$ about x-axis followed by inversion
24. Rotation of $-\pi/2$ about x-axis followed by inversion

b. Irreducible Representations

We list here a set of irreducible representations of the point group T_d. We stress that this set is not unique as any unitary transformation of a given irreducible representation provides another irreducible representation.

Representation A_1

$$\Gamma(R) = 1 \quad \text{for all} \quad R.$$

Representation A_2

$$\Gamma(R) = 1 \quad \text{for} \quad R \leq 12$$
$$\Gamma(R) = -1 \quad \text{for} \quad R \geq 13.$$

Representation E

$$\Gamma(R) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{for} \quad R = 1,2,3,4$$

$$\Gamma(R) = \begin{pmatrix} -1/2 & -3/2 \\ 3/2 & -1/2 \end{pmatrix} \quad \text{for} \quad R = 5,7,9,11$$

$$\Gamma(R) = \begin{pmatrix} -1/2 & -3/2 \\ 3/2 & -1/2 \end{pmatrix} \quad \text{for} \quad R = 6,8,10,11$$

$$\Gamma(R) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{for} \quad R = 13,14,19,20$$

$$\Gamma(R) = \begin{pmatrix} -1/2 & 3/2 \\ 3/2 & -1/2 \end{pmatrix} \quad \text{for} \quad R = 15,16,21,22$$

$$\Gamma(R) = \begin{pmatrix} -1/2 & -3/2 \\ -3/2 & 1/2 \end{pmatrix} \quad \text{for} \quad R = 17,18,23,24$$

<u>Representation T_1</u>

$$\Gamma(1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma(2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\Gamma(3) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \Gamma(4) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma(5) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad \Gamma(6) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(7) = \begin{pmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} \qquad \Gamma(8) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(9) = \begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} \qquad \Gamma(10) = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(11) = \begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad \Gamma(12) = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(13) = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \Gamma(14) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\Gamma(15) = \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \qquad \Gamma(16) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(17) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \qquad \Gamma(18) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\Gamma(19) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma(20) = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma(21) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \qquad \Gamma(22) = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(23) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \qquad \Gamma(24) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$$

<u>Represenation T_2</u>

$$\Gamma(1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma(2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\Gamma(3) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \Gamma(4) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma(5) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad \Gamma(6) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(7) = \begin{pmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} \qquad \Gamma(8) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(9) = \begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} \qquad \Gamma(10) = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(11) = \begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad \Gamma(12) = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(13) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma(14) = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma(15) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \qquad \Gamma(16) = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(17) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad \Gamma(18) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$\Gamma(19) = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \Gamma(20) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\Gamma(21) = \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \qquad \Gamma(22) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(23) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \qquad \Gamma(24) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

Appendix C

EXTENDED HÜCKEL PROGRAMS

1. Program to group equivalent pairs of atoms
2. Program to calculate overlap matrix
3. Program to calculate energy levels and eigenvectors

1. Program to group equivalent pairs of atoms

```
C       PROGRAM OBTAINED FROM D. FRANCESCHETTI, OCTOBER, 1977
C       MODIFIED BY D. MILLER AND C.SWARTS
C
C       THIS PROGRAM READS DATA FOR AND CALLS SUBROUTINE PAIR.
C
      COMMON/XYZ/X(250),Y(250),Z(250)
      COMMON/COEF/ NCF(10),NL(10),CO(10,10),EXPON(10,10),NPW(10,10),
     1KL(5,5),IX(5,5,8),IY(5,5,8),IZ(5,5,8),
     2 NA,KA,NAK(5)
      DIMENSION JTA(8),L1(10),L2(10),ID(12)
      DIMENSION NORB(5)
      CALL OPCLS(0)
      READ(21,1) NDIM,NA,NFUN,KA
1     FORMAT(8I5)
      READ(21,1) ((NAK(I),NORB(I)),I=1,KA)
      READ(21,9) (JTA(K),K=1,8),KD,NOL
      READ(21,8) AK
8     FORMAT(F5.2)
9     FORMAT(12I5)
      READ(21,9) ((L1(I),L2(I)),I=1,NOL)
      READ(21,9) (ID(J),J=1,KD)
      PRINT1,NDIM,NA,NFUN,KA
      DO 40 J=1,NFUN
      READ (21,7)    NCF(J),NL(J)
      PRINT 7,    NCF(J),NL(J)
    7 FORMAT(4I3,8I1,4I5,F5.2)
      NCJ=NCF(J)
      READ(21,41)      (CO(I,J),EXPON(I,J),NPW(I,J),I=1,NCJ)
      PRINT 41,    (CO(I,J),EXPON(I,J),NPW(I,J),I=1,NCJ)
   41 FORMAT(2F10.6,I5)
   40 CONTINUE
      DO 2 I=1,KA
      DO 2 J=I,KA
      READ (21,3)KL(I,J)
      PRINT3,KL(I,J)
      KLJ=KL(I,J)
      READ (21,3)(IX(I,J,K),IY(I,J,K),IZ(I,J,K),K=1,KLJ)
      PRINT3,(IX(I,J,K),IY(I,J,K),IZ(I,J,K),K=1,KLJ)
    3 FORMAT(24I3)
    2 CONTINUE
      READ (21,15)((X(I),Y(I),Z(I)),I=1,NA)
      PRINT15,((X(I),Y(I),Z(I)),I=1,NA)
   15 FORMAT(3F10.6)
    4 FORMAT(6I5)
      PRINT 4, NA,(NAK(I),I=1,KA)
      CALL PAIR
      CALL OPCLS(1)
      END
C
C
      SUBROUTINE OPCLS(K)
C      SUBROUTINE TO OPEN AND CLOSE FILES
      IF(K.EQ.1) GO TO 1
      OPEN(UNIT=21,DEVICE='DSK',FILE='INPUT.DAT',DIALOG)
      OPEN(UNIT=22,DEVICE='DSK',FILE='PAIROT.DAT',DIALOG)
```

```
      RETURN
    1 CONTINUE
      CLOSE(UNIT=21)
      CLOSE(UNIT=22)
      RETURN
      END
C
C
      SUBROUTINE FAIR
C      THIS SUBROUTINE GROUPS EQUIVALENT PAIRS OF ATOMS
C
      DIMENSION R(250,250),S(2500),T(2500),IC(5,5),NU(5)
      COMMON/XYZ/X(250),Y(250),Z(250)
      COMMON/COEF/NCF(10),NL(10),CO(10,10),EXPON(10,10),NPW(10,10),
     1KL(5,5),IX(5,5,8),IY(5,5,8),IZ(5,5,8),
     2 NATOM,NK,NAK(5)
1     FORMAT(6I5)

      N=0
      II=NATOM-1
      DO 10 I=1,II
      K=I+1
      DO 10 J=K,NATOM
      R(I,J)=(X(I)-X(J))**2+(Y(I)-Y(J))**2+(Z(I)-Z(J))**2
      N=N+1
      S(N)=R(I,J)
   10 PRINT 3,I,J,R(I,J)
    3 FORMAT(2I10,F20.6)
      DO 5 L=2,N
      DO 5 M=L,N
      IF(S(L-1)-S(M)) 5,5,6
    6 SS=S(M)
      S(M)=S(L-1)
      S(L-1)=SS
    5 CONTINUE
      JJ=1
      T(JJ)=S(1)
      DO 8 I=2,N
      IF(S(I)-S(I-1)) 8,8,9
    9 JJ=JJ+1
      T(JJ)=S(I)
    8 CONTINUE
      PRINT 1,N,JJ
      PRINT 7, (T(J),J=1,JJ)
    7 FORMAT(F20.6)
      NU(1)=NAK(1)
      DO 14 I=2,NK
   14 NU(I)=NU(I-1)+NAK(I)
      ISUM=0
      DO 11 MM=1,JJ
      DO 4 I=1,NK
      DO 4 J=1,NK
    4 IC(I,J)=0
      DO 11 I=1,II
      K=I+1
```

```
      DO 11 J=K,NATOM
      IF(R(I,J)-T(MM)) 11,12,11
   12 CONTINUE
        ITYPE=0
      DO 15 IK=1,NK
      ITYPE=IK
      IF(I-NU(IK)) 16,16,15
   15 CONTINUE
   16 DO 17 JK=ITYPE,NK
      JTYPE=JK
      IF(J-NU(JK)) 20,20,17
   17 CONTINUE
      GO TO 11
      GO TO 11
   20 IC(ITYPE,JTYPE)=IC(ITYPE,JTYPE)+1
        ISAME=1
        IF(IC(ITYPE,JTYPE).EQ.1) ISAME=0
   30 PRINT 50,I,J,ISAME,ITYPE,JTYPE,R(I,J)
      WRITE(22,40)  I,J,ISAME,ITYPE,JTYPE
      ISUM=ISUM+1
   40 FORMAT(5I3)
   50 FORMAT(5I3,F20.6)
   11 CONTINUE
      PRINT 1,ISUM
      RETURN
      END
```

2. Program to calculate overlap matrix

```
C       PROGRAM OBTAINED FROM D. FRANCESCHETTI, OCTOBER 1977
C          MODIFIED BY D. MILLER AND C. SWARTS
C
C         PROGRAM OVER1
C         MODIFIED TO SAVE STORAGE SEPT 75
C         MAKE FILE FOR09.DAT=FOR07.DAT(DATAOUTPUT),FOR02.DAT(PAIR
C         OUTPUT),FOR01.DAT(UNIMAT OUTPUT)
C         CALCULATES OVERLAP MATRIX AND PLACES IT IN BLOCK DIAGONAL
C         FORM
C         WRITES DIAGONAL BLOCKS ON F:3
C         WRITES THEIR EIGENVECTORS AND EIGENVALUES ON F:4
        DIMENSION SL(10000),UT(140,24),JAY(140,25),XV(140),
       1 EXTRA(50,50),UXTRA(50,50)
        DIMENSION X(50),Y(50),Z(50),L1(10),L2(10)
        DIMENSION NAK(5),NORB(5)
          DIMENSION JTA(8),SS(8),ID(12)
          DIMENSION BLK(1275)
        EQUIVALENCE (SL(1),EXTRA(1)),(SL(2501),UXTRA(1)),
       1(SL(5001),BLK(1))
        COMMON/KLY/NC(10),NL(10),CO(10,10),EXPON(10,10),NPW(10,10),
       1KL(5,5),IX(5,5,8),IY(5,5,8),IZ(5,5,8)
        REAL L,M,N
        CALL OPCLS(0)
        READ(27,7) NDIM,NATOM,NFUN,KA
        READ(27,7) ((NAK(I),NORB(I)),I=1,KA)
        READ(27,11) (JTA(K),K=1,8),KD,NOL
        READ(27,12) AK
          LEN=(NDIM*NDIM+NDIM)/2
 7      FORMAT(8I5)
 12     FORMAT(F5.2)
 13     FORMAT(2I3)
        READ (27,11) ((L1(I),L2(I)),I=1,NOL)
        PRINT11,((L1(I),L2(I)),I=1,NOL)
   11   FORMAT(12I5)
        READ (27,11)    (ID(J),J=1,KD)
        PRINT 11, (ID(J),J=1,KD)
    8   FORMAT(8F10.6)
        DO 40 J=1,NFUN
        READ (27,13) NC(J),NL(J)
        PRINT 7,    NC(J),NL(J)
        NCJ=NC(J)
        READ (27,41)  (CO(I,J),EXPON(I,J),NPW(I,J),I=1,NCJ)
        PRINT 41,     (CO(I,J),EXPON(I,J),NPW(I,J),I=1,NCJ)
   41   FORMAT(2F10.6,I5)
   40   CONTINUE
        DO 2 I=1,KA
        DO 2 J=I,KA
        READ (27,3) KL(I,J)
        PRINT3,KL(I,J)
        KLJ=KL(I,J)
        READ (27,3) (IX(I,J,K),IY(I,J,K),IZ(I,J,K),K=1,KLJ)
        PRINT 3,    (IX(I,J,K),IY(I,J,K),IZ(I,J,K),K=1,KLJ)
    3   FORMAT(24I3)
    2   CONTINUE
        READ (27,15) ((X(I),Y(I),Z(I)),I=1,NATOM)
```

```
      PRINT 15,   ((X(I),Y(I),Z(I)),I=1,NATOM)
   15 FORMAT(3F10.6)
      DO 17 J=1,KD
      I=ID(J)
      READ  (27,15),X(I),Y(I),Z(I)
   17 PRINT 15,X(I),Y(I),Z(I)
      DO 64 I=1,NATOM
      X(I)=X(I)/0.529177
      Y(I)=Y(I)/0.529177
      Z(I)=Z(I)/0.529177
   64 CONTINUE
      DO 20 I=1,LEN
   20 SL(I)=0.0
      DO 32 I=1,NDIM
        IND=(I*I+I)/2
   32 SL(IND)=1.0
      IATOM=NATOM*(NATOM-1)/2
      DO 28 IA=1,IATOM
      READ (22,1) I,J,ISAME,ITYPE,JTYPE
    1 FORMAT (5I3)
      D=((X(J)-X(I))**2+(Y(J)-Y(I))**2+(Z(J)-Z(I))**2)**0.5
      L=(X(J)-X(I))/D
      M=(Y(J)-Y(I))/D
      N=(Z(J)-Z(I))/D
      IF(ISAME) 42,42,45
   42 CONTINUE
      CALL OVER (D,SS,JTA,ITYPE,JTYPE)
      INDX=1+NORB(ITYPE)/4
      JNDX=1+NORB(JTYPE)/4
      GO TO (70,71,72)JNDX
   70 GO TO 43
   71 SS(2)=-SS(2)
      GO TO 43
   72 SS(2)=-SS(2)
      SS(7)=-SS(7)
      SS(8)=-SS(8)
      GO TO 43
   43 CONTINUE
      PRINT 123,(SS(KS),KS=1,5)
  123 FORMAT(5E14.7)
   45 CONTINUE
      CALL RST(L,M,N,I,J,SS,SL,NDIM,INDX,JNDX,KA,NAK,NORB)
   28 CONTINUE
      READ(25,75) NJP,NJMAX
      READ (25,65)  ((UT(I,J),J=1,NJMAX),I=1,NDIM)
C       PRINT 65,((UT(I,J),J=1,NJMAX),I=1,NDIM)
      READ (25,75) ((JAY(I,J),J=1,NJP),I=1,NDIM)
C       PRINT 75,((JAY(I,J),J=1,NJP),I=1,NDIM)
   75   FORMAT(9I8)
   65 FORMAT(8E14.7)
        DO 10 K=1,NOL
        L1K=L1(K)
        L2K=L2(K)
      CALL BLOCK (SL,UT,XV,JAY,NDIM,NJMAX,NJP,L1K,L2K)
   10 CONTINUE
```

```
      REWIND 35
C       IF THIS PROGRAM TAKES UP TOO MUCH ROOM, THIS IS A GOOD
C       PLACE TO BREAK IT INTO TWO PROGRAMS,EACH WITH A SMALLER
C       NUMBER OF SUBROUTINES. OTHERWISE YOU COULD BUILD A
C       TREE.
        DO 100 K=1,NOL
        LSIZE=L2(K)-L1(K)+1
        READ(35,202) LENGTH
  202   FORMAT(1X,I10)
        NN=LENGTH/200+1
        IF(MOD(LENGTH,200).EQ.0) NN=NN-1
        K1MAX=200
        DO 205 II=1,NN
        I1=1+200*(II-1)
        IF(II.EQ.NN) K1MAX=LENGTH-I1+1
        READ(35,200) (BLK(I),I=I1,K1MAX+I1-1)
  200   FORMAT(1X,8E14.7)
  205   CONTINUE
        CALL FILUP(EXTRA,BLK,LSIZE)
        WRITE (33,65) ((EXTRA(I,J),J=1,LSIZE),I=1,LSIZE)
        PRINT 1962
 1962 FORMAT(1H0,60X,15HOVERLAP MATRIX     )
        CALL PEGLEG(EXTRA,LSIZE,50)
        CALL HDIAG(EXTRA,LSIZE,0,UXTRA,NR,50)
        WRITE(34,65) ((UXTRA(I,J),J=1,LSIZE),I=1,LSIZE)
        DO 103 I=1,LSIZE
  103 WRITE (34,65) EXTRA(I,I)
        DO 505 I=1,LSIZE
        IF(EXTRA(I,I)) 502,502,505
  502 PRINT 503, I,I,EXTRA(I,I)
  503 FORMAT(1H0,50X,27HIMPOSSIBLE S EIGENVALUE S(   ,I3,1H,
     1 ,I3,4H) = ,F8.3)
      CALL OPCLS(1)
        CALL EXIT
  505 CONTINUE
  100 CONTINUE
      CALL OPCLS(1)
        CALL EXIT
        END
        INTEGER FUNCTION LOC(I,J)
        IX=I
        JX=J
        IF(IX-JX) 1,2,2
    1 KX=IX+(JX*JX-JX)/2
        GO TO 3
    2 KX=JX+(IX*IX-IX)/2
    3 LOC=KX
        RETURN
        END
        SUBROUTINE BLOCK(H,UT,H1,JAY,N,NT,NTP,L1,L2)
        DIMENSION H(10732),BLK(200),UT(N,NT),H1(N),JAY(N,NTP)
C       GET BLOCK OF SQUARE MATRIX FROM I,J=L1 TO I,J=L2.SINCE IT IS
C       SYMMETRIC,I=L1 TO J IS SUFFICIENT
        ICOUNT=0
  202   FORMAT(1H1,I10)
```

```
      NDIM=L2-L1+1
      LENGTH=(NDIM*NDIM+NDIM)/2
      WRITE(35,202) LENGTH
      DO 100 J=L1,L2
C     NOW J IS FIXED. FIRST GET JTH ROW OF UT*H
      KMAX=JAY(J,NTF)
      DO 20 L=1,N
      H1(L)=0.0
      DO 20 M=1,KMAX
   20 H1(L)=H1(L)+UT(J,M)*H(LOC(JAY(J,M),L))
C     THIS IS ALSO JTH COLUMN OF (UT*H) TRANSPOSE
C     IF WE MULTIPLY BY ITH ROW OF UT WE WILL GET HPRIME(I,J)
      DO 50 I=L1,J
      KMAX=JAY(I,NTF)
      HPRIME=0.0
      DO 40 K=1,KMAX
   40 HPRIME=HPRIME+UT(I,K)*H1(JAY(I,K))
C     NOW PUT IN PROPER PLACE IN ARRAY BLK
      ICOUNT=ICOUNT+1
      BLK(ICOUNT)=HPRIME
      IF(ICOUNT.LT.200) GO TO 50
      WRITE(35,200)( BLK(III),III=1,200)
      ICOUNT=0
   50 CONTINUE
  100 CONTINUE
      IF(ICOUNT.NE.0) WRITE (35,200) (BLK(I),I=1,ICOUNT)
  200 FORMAT(1H0,8E14.7)
      RETURN
      END
      SUBROUTINE FILUP(A,B,N)
      DIMENSION A(50,50)
      DIMENSION B(1)
C     TAKES THE N BY N MATRIX, STORED COMPRESSED IN BB
C     AND PUTS INTO A
      LENGTH =(N*N+N)/2
      I=1
      J=1
      DO 100 K=1,LENGTH
      A(I,J)=B(K)
      A(J,I)=B(K)
      I=I+1
      IF(I-J) 100,100,50
   50 I=1
      J=J+1
  100 CONTINUE
      RETURN
      END
      SUBROUTINE RST(L,M,N,I,J,SS,SL,NDIM,INDX,JNDX,KA,NAK,NORB)
      DIMENSION NAK(KA),NORB(KA)
      DIMENSION SS(8),SL(10000)
      REAL L,M,N
      KK=NDIM
      II=I-1
      IO=0
      DO 11 K=1,KA
```

```
      KI=K
      IF(II-NAK(K)) 12,13,13
   13 II=II-NAK(K)
   11 IO=IO+NAK(K)*NORB(K)
   12 JO=IO
      JJ=J-I+II
      DO 14 K=KI,KA
      KJ=K
      IF(JJ-NAK(K)) 15,15,16
   16 JJ=JJ-NAK(K)
   14 JO=JO+NAK(K)*NORB(K)
   15 IO=IO+II*NORB(KI)+1
      JO=JO+JJ*NORB(KJ)+1
      IF(INDX-JNDX) 10,10,9
    9 ID=IO
      IO=JO
      JO=ID
   10 CONTINUE
      I1=IO+1
      I2=IO+2
      I3=IO+3
      I4=IO+4
      I5=IO+5
      I6=IO+6
      I7=IO+7
      I8=IO+8
      J1=JO+1
      J2=JO+2
      J3=JO+3
      J4=JO+4
      J5=JO+5
      J6=JO+6
      J7=JO+7
      J8=JO+8
      IJDX=LOC(INDX,JNDX)
      GO TO (1,2,3,4,5,6) IJDX
    1 CONTINUE
      SL(LOC(I,J))=SS(1)
      GO TO 7
    2 CONTINUE
      SL(LOC(IO,JO))=SS(1)
      SL(LOC(IO,J1))=L*SS(2)
      SL(LOC(IO,J2))=M*SS(2)
      SL(LOC(IO,J3))=N*SS(2)
      GO TO 7
    4 CONTINUE
      SL(LOC(IO,J4))=3.0**0.5*L*M*SS(3)
      SL(LOC(IO,J5))=3.0**0.5*M*N*SS(3)
      SL(LOC(IO,J6))=3.0**0.5*N*L*SS(3)
      SL(LOC(IO,J7))=0.5*3.0**0.5*(L*L-M*M)*SS(3)
      SL(LOC(IO,J8))=(N*N-0.5*(L*L+M*M))*SS(3)
      GO TO 2
    3 CONTINUE
      SL(LOC(I1,JO))=L*SS(3)
      SL(LOC(I1,J1))=L*L*SS(4)+(1.0-L*L)*SS(5)
```

```
      SL(LOC(I1,J2))=L*M*SS(4)-L*M*SS(5)
      SL(LOC(I2,J1))=SL(LOC(I1,J2))
      SL(LOC(I1,J3))=L*N*SS(4)-L*N*SS(5)
      SL(LOC(I3,J1))=SL(LOC(I1,J3))
      SL(LOC(I2,J0))=M*SS(3)
      SL(LOC(I2,J2))=M*M*SS(4)+(1.0-M*M)*SS(5)
      SL(LOC(I2,J3))=M*N*SS(4)-M*N*SS(5)
      SL(LOC(I3,J2))=SL(LOC(I2,J3))
      SL(LOC(I3,J0))=N*SS(3)
      SL(LOC(I3,J3))=N*N*SS(4)+(1.0-N*N)*SS(5)
      GO TO 2
    5 CONTINUE
      SL(LOC(I1,J0))=L*SS(4)
      SL(LOC(I1,J1))=L*L*SS(5)+(1.0-L*L)*SS(6)
      SL(LOC(I1,J2))=L*M*SS(5)-L*M*SS(6)
        SL(LOC(I2,J1))=SL(LOC(I1,J2))
      SL(LOC(I1,J3))=L*N*SS(5)-L*N*SS(6)
        SL(LOC(I3,J1))=SL(LOC(I1,J3))
      SL(LOC(I1,J4))=3.0**0.5*L*L*M*SS(7)+M*(1.0-2.0*L*L)*SS(8)
      SL(LOC(I1,J5))=3.0**0.5*L*M*N*SS(7)-2.0*L*M*N*SS(8)
      SL(LOC(I1,J6))=3.0**0.5*L*L*N*SS(7)+N*(1.0-2.0*L*L)*SS(8)
        SL(LOC(I1,J7)) =0.5*3.0**0.5*L*(L*L-M*M)*
     1SS(7)+L*(1.0-L*L+M*M)*SS(8)
      SL(LOC(I1,J8))=L*(N*N-0.5*(L*L+M*M))*SS(7)-3.0**0.5*L*N*N*SS(8)
      SL(LOC(I2,J0))=M*SS(4)
      SL(LOC(I2,J2))=M*M*SS(5)+(1.0-M*M)*SS(6)
      SL(LOC(I2,J3))=M*N*SS(5)-M*N*SS(6)
        SL(LOC(I3,J2))=SL(LOC(I2,J3))
      SL(LOC(I2,J4))=3.0**0.5*L*M*M*SS(7)+L*(1.0-2.0*M*M)*SS(8)
      SL(LOC(I2,J5))=3.0**0.5*M*M*N*SS(7)+N*(1.0-2.0*M*M)*SS(8)
      SL(LOC(I2,J6))=3.0**0.5*L*M*N*SS(7)-2.0*L*M*N*SS(8)
      SL(LOC(I2,J7))=0.5*3.0**0.5*M*(L*L-M*M)*
     1SS(7)-M*(1.0+L*L-M*M)*SS(8)
      SL(LOC(I2,J8))=M*(N*N-0.5*(L*L+M*M))*SS(7)-3.0**0.5*M*N*N*SS(8)
      SL(LOC(I3,J0))=N*SS(4)
      SL(LOC(I3,J3))=N*N*SS(5)+(1.0-N*N)*SS(6)
      SL(LOC(I3,J4))=3.0**0.5*L*M*N*SS(7)-2.0*L*M*N*SS(8)
      SL(LOC(I3,J5))=3.0**0.5*N*N*M*SS(7)+M*(1.0-2.0*N*N)*SS(8)
      SL(LOC(I3,J6))=3.0**0.5*N*N*L*SS(7)+L*(1.0-2.0*N*N)*SS(8)
      SL(LOC(I3,J7))=0.5*3.0**0.5*N*(L*L-M*M)*SS(7)-N*(L*L-M*M)*SS(8)
      SL(LOC(I3,J8))=N*(N*N-0.5*(L*L+M*M))*
     1SS(7)+3.0**0.5*N*(L*L+M*M)*SS(8)
      GO TO 4
    6 SL(LOC(I4,J0))=3.0**0.5*L*M*SS(9)
      SL(LOC(I5,J0))=3.0**0.5*M*N*SS(9)
      SL(LOC(I6,J0))=3.0**0.5*L*N*SS(9)
      SL(LOC(I7,J0))=0.5*3.0**0.5*(L*L-M*M)*SS(9)
      SL(LOC(I8,J0))=(N*N-0.5*(L*L+M*M))*SS(9)
      SL(LOC(I4,J1))=3.0**0.5*L*L*M*SS(10)+M*(1.0-2.0*L*L)*SS(11)
      SL(LOC(I5,J1))=3.0**0.5*L*M*N*SS(10)-2.0*L*M*N*SS(11)
      SL(LOC(I6,J1))=3.0**0.5*L*L*N*SS(10)+N*(1.0-2.0*L*L)*SS(11)
      SL(LOC(I7,J1))=0.5*3.0**0.5*L*(L*L-M*M)*SS(10)+L*(1.0-L*L+M*M)*
     1SS(11)
      SL(LOC(I8,J1))=L*(N*N-0.5*(L*L+M*M))*SS(10)-3.0**0.5*L*N*N
     1*SS(11)
```

```
      SL(LOC(I4,J2))=3.0**0.5*L*M*M*SS(10)+L*(1.0-2.0*M*M)*SS(11)
      SL(LOC(I5,J2))=3.0**0.5*M*M*N*SS(10)+N*(1.0-2.0*M*M)*SS(11)
      SL(LOC(I6,J2))=3.0**0.5*L*M*N*SS(10)-2.0*L*M*N*SS(11)
      SL(LOC(I7,J2))=0.5*3.0**0.5*M*(L*L-M*M)*SS(10)-M*(1.0+L*L-M*M)*
     1SS(11)
      SL(LOC(I8,J2))=M*(N*N-0.5*(L*L+M*M))*SS(10)-3.0**0.5*M*N*N*
     1SS(11)
      SL(LOC(I4,J3))=3.0**0.5*L*M*N*SS(10)-2.0*L*M*N*SS(11)
      SL(LOC(I5,J3))=3.0**0.5*N*N*M*SS(10)+M*(1.0-2.0*N*N)*SS(11)
      SL(LOC(I6,J3))=3.0**0.5*N*N*L*SS(10)+L*(1.0-2.0*N*N)*SS(11)
      SL(LOC(I7,J3))=0.5*3.0**0.5*N*(L*L-M*M)*SS(10)-N*(L*L-M*M)*
     1SS(11)
      SL(LOC(I8,J3))=N*(N*N-0.5*(L*L+M*M))*SS(10)+3.0**0.5*N*(L*L
     1+M*M)*SS(11)
      SL(LOC(I4,J4))=3.0*L*L*M*M*SS(12)+(N*N+L*L*M*M)*SS(14)+
     1(L*L+M*M-4.0*L*L*M*M)*SS(13)
      SL(LOC(I5,J4))=3.0*L*M*M*M*N*SS(12)+(M*M*L*N-L*N)*SS(14)+
     1(L*N-4.0*L*M*M*N)*SS(13)
      SL(LOC(I6,J4))=3.0*L*L*M*N*SS(12)+(L*L*M*N-L*N)*SS(14)+
     1(M*N-4.0*L*L*M*N)*SS(13)
      SL(LOC(I7,J4))=L*M*(L*L-M*M)*(1.5*SS(12)+0.5*SS(14)-2.0*SS(13))
      SL(LOC(I8,J4))=0.5*3.0**0.5*(L*M*(3.0*N*N-1.0)*SS(12)+
     1(L*M+L*M*N*N)*SS(14)-4.0*L*M*N*N*SS(13))
      SL(LOC(I4,J5))=SL(LOC(I5,J4))
      SL(LOC(I5,J5))=3.0*M*M*N*N*SS(12)+(L*L+M*M*N*N)*SS(14)+
     1(M*M+N*N-4.0*M*M*N*N)*SS(13)
      SL(LOC(I6,J5))=3.0*L*M*N*N*SS(12)+(L*M*N*N-L*M)*SS(14)+
     1(L*M-4.0*L*M*N*N)*SS(13)
      SL(LOC(I7,J5))=3.0*M*N*(L*L-M*M)*SS(12)+M*N*(1.0+0.5*(L*L-
     1M*M))*SS(14)-(M*N*(1.0+L*L-M*M))*SS(13)
      SL(LOC(I8,J5))=0.5*3.0**0.5*(L*M*(3.0*N*N-1.0)*SS(12)+3.0*
     1(L*M+L*M*N*N)*SS(14)-4.0*L*M*N*N*SS(13))
      SL(LOC(I4,J6))=SL(LOC(I6,J4))
      SL(LOC(I5,J6))=SL(LOC(I6,J5))
      SL(LOC(I6,J6))=3.0*L*L*N*N*SS(12)+(M*M+L*L*N*N)*SS(14)+
     1(L*L+N*N-4.0*L*L*N*N)*SS(13)
      SL(LOC(I7,J6))=3.0*L*N*(L*L-M*M)*SS(12)+L*N*(L*L-M*M-1.0)*SL
     1(14)+L*N*(1.0-2.0*(L*L-M*M))*SS(13)
      SL(LOC(I8,J6))=3.0**0.5*L*N*((3.0*N*N-1.0)*SS(12)+(0.5*N*N-1.0)
     1*SS(14)+(1-2.0*N*N)*SS(13))
      SL(LOC(I4,J7))=SL(LOC(I7,J4))
      SL(LOC(I5,J7))=SL(LOC(I7,J5))
      SL(LOC(I6,J7))=SL(LOC(I7,J6))
      SL(LOC(I7,J7))=3.0*(L*L-M*M)**2*SS(12)+(0.25*(L*L-M*M)**2+N*N)*
     1SS(14)+(L*L+M*M)*SS(13)
      SL(LOC(I7,J8))=0.5*3.0**0.5*((L*L-M*M)*(3.0*N*N-1.0)*SS(12)+
     1(L*L-M*M)*0.5*(1.0-N*N)*SS(14)+4.0*N*N*(M*M-L*L)*SS(13))
      SL(LOC(I4,J8))=SL(LOC(I8,J4))
      SL(LOC(I5,J8))=SL(LOC(I8,J5))
      SL(LOC(I6,J8))=SL(LOC(I8,J6))
      SL(LOC(I7,J8))=SL(LOC(I8,J7))
      SL(LOC(I8,J8))=0.25*(3.0*N*N-1.0)*2*SS(12)+0.75*(1.0-N*N)**2*
     1SS(14)+3.0*(1.0-N*N)*N*N*SS(14)
      GO TO 5
    7 CONTINUE
```

```
      RETURN
      END
      SUBROUTINE OVER (D,SS,JTA,ITYPE,JTYPE)
      DIMENSION SS(8)
      DIMENSION RAA(15),RBB(15),ZZZ(8),QQQ(8),ITA(8),JTA(8)
      DIMENSION CO1(10),CO2(10),EXPON1(10),EXPON2(10),NPW1(10),
     1NPW2(10)
      COMMON/KLY/NC(10),NL(10),CO(10,10),EXPON(10,10),NPW(10,10),
     1KL(5,5),IX(5,5,8),IY(5,5,8),IZ(5,5,8)
      COMMON/BEGHO/RAA,RBB,ZZZ,ITA,R,EX1,EX2,X,NA,NB,LA,LB,M,IT,ITAX,
     1KRN,LRN,IAF,IBF,LLB,IEN,JPX,IPX,JNA,JNB,NCIH,IJKSWH,AN,BN
      R=D
      DO 27 I=1,8
   27 ITA(I)=JTA(I)
      KLI=KL(ITYPE,JTYPE)
      DO 6 KK=1,KLI
      I=IX(ITYPE,JTYPE,KK)
      J=IY(ITYPE,JTYPE,KK)
      M=IZ(ITYPE,JTYPE,KK)
      IF(I) 15,15,14
   15 SS(KK)=SS(KK-1)
      GO TO 6
   14 NC1=NC(I)
      LA=NL(I)
      NC2=NC(J)
      LB=NL(J)
      DO 12 K=1,NC1
      CO1(K)=CO(K,I)
      EXPON1(K)=EXPON(K,I)
   12 NPW1(K)=NPW(K,I)
      DO 13 K=1,NC2
      CO2(K)=CO(K,J)
      EXPON2(K)=EXPON(K,J)
   13 NPW2(K)=NPW(K,J)
      IJKSWH=0
      IF(LA-LB) 50,50,51
   51 LC=LA
      LA=LB
      LB=LC
      IJKSWH=1
   50 CONTINUE
      DO 2 I=1,8
      ZZZ(I)=0.0
    2 QQQ(I)=0.0
      DO 3 I=1,NC1
      DO 3 J=1,NC2
      NA=NPW1(I)
      NB=NPW2(J)
      EX1=EXPON1(I)
      EX2=EXPON2(J)
      CALL OVRLPX
      DO 3 K=1,8
    3 QQQ(K)=QQQ(K)+CO1(I)*CO2(J)*ZZZ(K)
      SS(KK)=QQQ(1)
    6 CONTINUE
```

```
      RETURN
      END
      SUBROUTINE OVRLPX
      DIMENSION RAA(15),RBB(15),ZZZ(8),ITA(8)
      COMMON/BEGHO/RAA,RBB,ZZZ,ITA,R,EX1,EX2,X,NA,NB,LA,LB,M,IT,ITAX,
     1KRN,LRN,IAF,IBF,LLB,IEN,JPX,IPX,JNA,JNB,NCIH,IJKSWH,AN,BN
      CALL HARTZX
    3 CALL OFFENX
      CALL GOETCX
      IF(KRN-LRN) 3,4,4
    4 RETURN
      END
      SUBROUTINE HARTZX
      DIMENSION RAA(15),RBB(15),ZZZ(8),ITA(8)
      COMMON/BEGHO/RAA,RBB,ZZZ,ITA,R,EX1,EX2,X,NA,NB,LA,LB,M,IT,ITAX,
     1KRN,LRN,IAF,IBF,LLB,IEN,JPX,IPX,JNA,JNB,NCIH,IJKSWH,AN,BN
    1 LRN=0
      DO 3 J=1,8
      IF(ITA(J))4,3,4
    4 ITA(J)=1
    3 LRN=LRN+ITA(J)
      ML=0
      DO 7 ITAX=1,8
      ML=ML+ITA(ITAX)
      IF(ML-1) 7,6,6
    7 CONTINUE
    6 IT=ITAX-1
      MP=1
      IT=IT/2
      IEN=1
      IAF=0
      IBF=0
      NCIH=0
      IF(IJKSWH.EQ.0) GO TO 50
      I=NA
      NA=NB
      NB=I
      X=EX1
      EX1=EX2
      EX2=X
      I=ITA(3)
      ITA(3)=ITA(4)
      ITA(4)=I
   50 IF(LRN-1) 8,8,110
    8 IF(IT-1) 10,9,10
    9 MP=0
   10 LLB=NA+NB+MP+2
      IF(IT-2) 131,11,11
   11 ITA(1)=1
      GO TO 1
  110 MC=0
      DO 111 II=5,8
  111 MC=MC+ITA(II)
      LLB=NA+NB+3
      IF(MC) 131,131,113
```

```
113 LLB=LLB+2
131 KRN=0
    RETURN
    END
    SUBROUTINE OFFENX
    DIMENSION RAA(15),RBB(15),ZZZ(8),ITA(8)
    COMMON/BEGHO/RAA,RBB,ZZZ,ITA,R,EX1,EX2,X,NA,NB,LA,LB,M,IT,ITAX,
   1KRN,LRN,IAF,IBF,LLB,IEN,JPX,IPX,JNA,JNB,NCIH,IJKSWH,AN,BN
    LS=NA+NB+5
    IF(IAF+IBF)4,4,66
  4 KRN=KRN+1
    IF(KRN-1) 131,131,13
 13 IEN=2
    ML=0
    DO 7 ITAX=1,8
    ML=ML+ITA(ITAX)
    IF(KRN-ML) 6,6,7
  7 CONTINUE
  6 IT=ITAX-1
    IT=IT/2
    NCIH=0
    IF(IT-2) 131,16,17
 16 IAF=ITAX-4
    IBF=IAF
    GO TO 18
 17 IAF=2*(8-ITAX)
    IBF=2*(ITAX-7)
 18 DO 21 LZ=3,LS
    LL=LZ-IAF
    RAA(LL)=RAA(LZ)
    LL=LZ-IBF
 21 RBB(LL)=RBB(LZ)
    NCIH=2
    IF(ITAX-5) 131,23,131
 23 NCIH=1
131 RETURN
 66 DO 61 LZ=3,LS
    MZ=LS-LZ+3
    LL=MZ-IAF
    RAA(MZ)=RAA(LL)
    LL=MZ-IBF
 61 RBB(MZ)=RBB(LL)
    IAF=0
    IBF=0
    GO TO 4
    END
    SUBROUTINE GOETCX
    DIMENSION RAA(15),RBB(15),ZZZ(8),ITA(8)
    COMMON/BEGHO/RAA,RBB,ZZZ,ITA,R,EX1,EX2,X,NA,NB,LA,LB,M,IT,ITAX,
   1KRN,LRN,IAF,IBF,LLB,IEN,JPX,IPX,JNA,JNB,NCIH,IJKSWH,AN,BN
    GO TO (15,6),IEN
 15 ALPH=0.5*R*(EX1+EX2)
    AN=SQRT((2.0*EX1)**(2*NA+1)/FACK(2*NA))
    BN=SQRT((2.0*EX2)**(2*NB+1)/FACK(2*NB))
    BETA=0.5*R*(EX1-EX2)
```

```
      XAMI=EXP(-ALPH)
      XBMI=EXP(-BETA)
      ABBETA=ABS(BETA)
      RAA(3)=XAMI/ALPH
      NBF2=LLB-3
      IF(ABBETA-3.0) 17,17,20
   20  RBB(3)=BFX(0,BETA,XBMI)
      GO TO 102
   17 RBB(LLB)=BFX(NBF2,BETA,XBMI)
      XMITTN=-1.0
      XIP=LLB
      XIP=XIP/2.0
      XJP=LLB/2
      IF(XIP-XJP-0.1) 102,102,103
  102 XMITTN=1.0
  103 DO 2 I=1,NBF2
      XMITTN=-1.0*XMITTN
      J=LLB-I
      XJP=I
      XIP=NBF2-I+1
      K=I+3
      IF(ABBETA-3.0) 27,27,30
   30 RBB(K)=(1.0/BETA)*(XMITTN/XBMI-XBMI+XJP*RBB(K-1))
      GO TO 2
   27 RBB(J)=(1.0/XIP)*(BETA*RBB(J+1)+XBMI-XMITTN/XBMI)
    2 RAA(I+3)=(1.0/ALPH)*(XAMI+XJP*RAA(I+2))
    6 JNA=NA
      JNB=NB
      IF(ITAX-2) 7,8,9
    7 CALL GENOVX
      ZZZ(ITAX)=X
      GO TO 1001
    8 NSW=0
      RSW=0.0
      IF(NA-LA-1) 91,91,89
   89 IF(NB-LB-1) 90,90,93
   90 NSW=1
      RSW=1.0
   91 COF=0.0
      GO TO 94
   93 G=(NA+LA)*(NA-LA-1)
      JNA=NA-2
      CALL GENOVX
      COF=-0.5*X*G
   94 G=2*NA*(1-NSW)+2*NB*NSW
      EEX=EX1*(1.0-RSW)+EX2*RSW
      JNA=NA-1+NSW
      JNB=NB-NSW
      CALL GENOVX
      COFF=0.5*G*X*EEX
      JNA=NA
      JNB=NB
      CALL GENOVX
      G=-0.5*EEX*EEX*X
      ZZZ(2)=G+COFF+COF
```

```
      GO TO 1001
    9 IA=1
      IB=0
      IF(ITAX-4) 10,11,7
   11 IA=0
      IB=1
   10 JNA=NA-IA
      JNB=NB-IB
      CALL GENOVX
      ZZZ(ITAX)=X
 1001 RETURN
      END
      SUBROUTINE GENOVX
      DIMENSION RAA(15),RBB(15),ZZZ(8),ITA(8)
      COMMON/BEGHO/RAA,RBB,ZZZ,ITA,R,EX1,EX2,X,NA,NB,LA,LB,M,IT,ITAX,
     1KRN,LRN,IAF,IBF,LLB,IEN,JPX,IPX,JNA,JNB,NCIH,IJKSWH,AN,BN
      SQT=1.7320508
      SQR=2.236068
      IPX=JNA-LA
      JPX=JNB-LB
      K=3*LA+LB+2*M+1
      G=0.5*AN*BN*((0.5*R)**(JNA+JNB+NCIH+1))
      GO TO (1,2,3,4,5,6,7,8,9,10,11,12,13),K
    1 X=RIIEX(0,0)
      GO TO 16
    2 X=SQT*(RIIEX(0,0)-RIIEX(1,1))
      GO TO 16
    3 X=(3.0*(RIIEX(0,0)+RIIEX(2,2))-4.0*RIIEX(1,1)-RIIEX(0,2)-RIIEX
     1(2,0))*0.5*SQR
      GO TO 16
      CALL OPCLS(1)
    4 CALL EXIT
    5 X=-3.0*(RIIEX(0,0)-RIIEX(2,2))
      GO TO 16
    6 X=-0.5*SQT*SQR*(3.0*(RIIEX(0,0)+RIIEX(3,3))-RIIEX(1,1)-RIIEX
     1(2,2) -RIIEX(0,2)-RIIEX(2,0)-RIIEX(3,1)-RIIEX(1,3))
      GO TO 16
    7 X=1.5*(RIIEX(2,0)+RIIEX(0,2)-RIIEX(0,0)-RIIEX(2,2))
      GO TO 16
    8 X=1.5*SQR*(RIIEX(3,3)+RIIEX(1,1)-RIIEX(3,1)-RIIEX(1,3)-RIIEX
     1(2,2)+RIIEX(2,0)+RIIEX(0,2)-RIIEX(0,0))
      GO TO 16
    9 X=1.25*(9.0*(RIIEX(0,0)+RIIEX(4,4))-6.0*(RIIEX(2,4)+RIIEX(4,2)
     1  +RIIEX(2,0)+RIIEX(0,2))+RIIEX(4,0)+RIIEX(0,4)+4.0*RIIEX(2,2))
      GO TO 16
      CALL OPCLS(1)
   10 CALL EXIT
   11 X=-7.5*(RIIEX(4,4)-RIIEX(4,2)-RIIEX(2,4)+RIIEX(2,0)+RIIEX(0,2)
     1 -RIIEX(0,0))
      GO TO 16
      CALL OPCLS(1)
   12 CALL EXIT
   13 X=1.875*(RIIEX(0,0)+RIIEX(4,4)+RIIEX(0,4)+RIIEX(4,0)+4.0*RIIEX
     1(2,2)-2.0*(RIIEX(0,2)+RIIEX(2,0)+RIIEX(2,4)+RIIEX(4,2)))
   16 X=X*G
```

```
      RETURN
      END
      FUNCTION RIIEX(MRI,NRI)
      DIMENSION RAA(15),RBB(15),ZZZ(8),ITA(8)
      COMMON/BEGHO/RAA,RBB,ZZZ,ITA,R,EX1,EX2,X,NA,NB,LA,LB,M,IT,ITAX,
     1KRN,LRN,IAF,IBF,LLB,IEN,JPX,IPX,JNA,JNB,NCIH,IJKSWH,AN,BN
      S=0.0
      KQ=MRI+1
      LRI=MRI+IPX+JPX+1
      DO 1 KRI=KQ,LRI
      MMM=LRI+NRI-KRI+3
      KRIMRI=KRI-KQ
    1 S=S+RAA(KRI+2)*RBB(MMM)*RMPEX(KRIMRI)
      RIIEX=S
      RETURN
      END
      FUNCTION RMPEX(KRIMRI)
      DIMENSION RAA(15),RBB(15),ZZZ(8),ITA(8)
      COMMON/BEGHO/RAA,RBB,ZZZ,ITA,R,EX1,EX2,X,NA,NB,LA,LB,M,IT,ITAX,
     1KRN,LRN,IAF,IBF,LLB,IEN,JPX,IPX,JNA,JNB,NCIH,IJKSWH,AN,BN
      RMPEXX=0.0
      LRM=JPX+1
      DO 1 I=1,LRM
      J=I-1
      NRMM=JPX
      MRMM=JPX-J
      A=RMMEX(NRMM,MRMM)
      NRMM=IPX
      MRMM=KRIMRI+J-JPX
    1 RMPEXX=RMPEXX+A*ABS(RMMEX(NRMM,MRMM))
      RMPEX=RMPEXX
      RETURN
      END
      FUNCTION RMMEX(NRMM,MRMM)
      IF(MRMM-NRMM) 1,2,3
    3 RMMEX=0.0
      GO TO 5
    2 RMMEX=1.0
      GO TO 5
    1 RMMEXX=1.0
      LAP=NRMM-MRMM
      A=NRMM
      DO 4 I=1,LAP
      RAP=I
    4 RMMEXX=-RMMEXX*(A-RAP+1.0)/RAP
    6 RMMEX=RMMEXX
    5 RETURN
      END
      FUNCTION FACK(N)
      FACKX=1.0
      IF(N) 11,11,1
    1 DO 2 J=1,N
      CC=J
    2 FACKX=FACKX*CC
   11 FACK=FACKX
```

```
      RETURN
      END
      FUNCTION BFX(N,BETA,XBMI)
      ABBETA=ABS(BETA)
      IF(ABBETA-.001) 901,904,904
  901 G=N/2
      F=N
      F=F/2.0
      IF(F-G-0.1) 902,902,903
  902 BFX=1.0/(F+0.5)
      GO TO 924
  903 BFX=0.0
      GO TO 924
  904 IF(N) 920,920,905
  905 IF(ABBETA-2.5) 906,906,920
  906 B=-ABBETA
      T1=1.0
      T2=1.0
      S1=1.0
      S2=1.0
      DO 907 I=1,N
      F=I
      T1=T1*ABBETA/F
      T2=T2*B/F
      S1=S1+T1
  907 S2=S2+T2
      T1=T1*ABBETA/(F+1.0)
      FN=T1
      S3=T1
      T2=T2*B/(F+1.0)
      S4=T2
      I=N+2
      F=I
  908 T1=T1*ABBETA/F
      S3=S3+T1
      I=I+1
      F=I
      IF(T1/S3-1.0E-09) 909,908,908
  909 I=N+2
      RN=N+1
      F=I
  910 T2=T2*B/F
      S4=S4+T2
      I=I+1
      F=I
      IF(ABS(T2/S4)-1.0E-08) 911,910,910
  911 T2=(S3*S2-S1*S4)/(FN*RN)
      BFX=T2
      IF(BETA) 912,912,924
  912 BFX=ABS(T2)
      GO TO 924
  920 XP=1.0/XBMI
      T2=(XP-XBMI)/BETA
      BFX=T2
      IF(N) 924,924,922
```

```
922 F=1.0
    DO 923 I=1,N
    F=-1.0*F
    G=I
923 T2=(F*XP-XBMI+G*T2)/BETA
    BFX=T2
924 RETURN
    END
    SUBROUTINE OPCLS(K)
    IF(K.EQ.1) GO TO 1
    OPEN(UNIT=27,DEVICE='DSK',FILE='GASP17.DAT',DIRECTORY='4,103'
   1,DIALOG)
    OPEN(UNIT=22,DEVICE='DSK',FILE='FAIR17.DAT',DIRECTORY='4,103'
   1,DIALOG)
    OPEN(UNIT=25,DEVICE='DSK',FILE='UGPN17.DAT',DIRECTORY='4,103'
   1,DIALOG)
    OPEN(UNIT=35,DEVICE='DSK',FILE='BLOCK.DAT')
    OPEN(UNIT=33,DEVICE='DSK',FILE='SGPN17.DAT',DIALOG)
    OPEN(UNIT=34,DEVICE='DSK',FILE='HGPN17.DAT',DIALOG)
    RETURN
  1 CONTINUE
    CLOSE(UNIT=27)
    CLOSE(UNIT=22)
    CLOSE(UNIT=25)
    CLOSE(UNIT=35)
    CLOSE(UNIT=33)
    CLOSE(UNIT=34)
    RETURN
    END
```

```
C       PROGRAM OBTAINED FROM D. FRANCESCHETTI, OCTOBER, 1977
C
      SUBROUTINE PEGLEG(A,N,NDIM)
      DIMENSION A(NDIM,NDIM)
C     MATRIX OUTPUT SUBROUTINE
   18 FORMAT(I4,3X,14F8.4)
   19 FORMAT(  1H0/1H0,14(5X,I3))
        I=NDIM
      KITE=0
   20 LOW=KITE+1
      KITE=KITE+14
      KITE=MIN0(KITE,N)
      WRITE (36,19)(I,I=LOW,KITE)
      DO 32 I=1,N
   32 WRITE (36,18)(I,(A(I,J),J=LOW,KITE))
      IF(N-KITE) 40,40,20
   40 RETURN
      END
      SUBROUTINE HDIAG(H,N,IEGEN,U,NR,NDIM)
C     MIHDI3, FORTRAN II DIAGONALIZATION OF A REAL SYMMETRIC MATRIX
C        BY THE JACOBI METHOD.
C     CALLING SEQUENCE FOR DIAGONALIZATION
C           CALL  HDIAG( H, N, IEGEN, U, NR)
C            WHERE H IS THE ARRAY TO BE DIAGONALIZED.
C     N IS THE ORDER OF THE MATRIX, H.
C
C     IEGEN MUST BE SET UNEQUAL TO ZERO IF ONLY EIGENVALUES ARE
C            TO BE COMPUTED.
C     IEGEN MUST BE SET EQUAL TO ZERO IF EIGENVALUES AND EIGENVECTORS
C            ARE TO BE COMPUTED.
C
C     U IS THE UNITARY MATRIX USED FOR FORMATION OF THE EIGENVECTORS.
C
C     NR IS THE NUMBER OF ROTATIONS.
C
C     A DIMENSION STATEMENT MUST BE INSERTED IN THE SUBROUTINE.
C     DIMENSION H(N,N), U(N,N), X(N), IQ(N)
C
C     SUBROUTINE PLACES COMPUTER IN THE FLOATING TRAP MODE
C
C     THE SUBROUTINE OPERATES ONLY ON THE ELEMENTS OF H THAT ARE TO
C            THE RIGHT OF THE MAIN DIAGONAL.  THUS, ONLY A TRIANGULAR
C            SECTION NEED BE STORED IN THE ARRAY H.
C
      DIMENSION H(NDIM,NDIM), U(NDIM,NDIM), X(150), IQ(150)
C
        I=NDIM
      IF (IEGEN) 15,10,15
   10 DO 14 I=1,N
      DO 14 J=1,N
      IF(I-J)12,11,12
   11 U(I,J)=1.0
      GO TO 14
   12 U(I,J)=0.
   14 CONTINUE
```

```
C
 15    NR = 0
       IF (N-1) 1000,1000,17
C
C      SCAN FOR LARGEST OFF DIAGONAL ELEMENT IN EACH ROW
C      X(I) CONTAINS LARGEST ELEMENT IN ITH ROW
C      IQ(I) HOLDS SECOND SUBSCRIPT DEFINING POSITION OF ELEMENT
C
 17    NMI1=N-1
       DO 30 I=1,NMI1
       X(I) = 0.
       IPL1=I+1
       DO 30 J=IPL1,N
       IF ( X(I) - ABS( H(I,J))) 20,20,30
 20    X(I)=ABS(H(I,J))
       IQ(I)=J
 30    CONTINUE
C
C      SET INDICATOR FOR SHUT-OFF.RAP=2**-27,NR=NO. OF ROTATIONS
       RAP=.745058059E-08
       HDTEST=1.0E38
C
C      FIND MAXIMUM OF X(I) S FOR PIVOT ELEMENT AND
C      TEST FOR END OF PROBLEM
C
 40    DO  70  I=1,NMI1
       IF (I-1) 60,60,45
 45    IF ( XMAX- X(I)) 60,70,70
 60    XMAX=X(I)
       IPIV=I
       JPIV=IQ(I)
 70    CONTINUE
C
C      IS MAX. X(I) EQUAL TO ZERO, IF LESS THAN HDTEST, REVISE HDTEST
       IF ( XMAX) 1000,1000,80
 80    IF (HDTEST) 90,90,85
 85    IF (XMAX - HDTEST) 90,90,148
 90    HDIMIN = ABS( H(1,1) )
       DO 110  I= 2,N
       IF (HDIMIN- ABS( H(I,I))) 110,110,100
 100   HDIMIN=ABS(H(I,I))
 110   CONTINUE
C
       HDTEST=HDIMIN*RAP
C
C      RETURN IF MAX.H(I,J)LESS THAN(2**-27)ABSF(H(K,K)-MIN)
       IF (HDTEST- XMAX) 148,1000,1000
 148   NR = NR+1
C
C      COMPUTE TANGENT, SINE AND COSINE,H(I,I),H(J,J)
 150   TANG=SIGN(2.0,(H(IPIV,IPIV)-H(JPIV,JPIV)))*H(IPIV,JPIV)/(ABS(
      1H(IPIV,IPIV)-H(JPIV,JPIV))+SQRT((H(IPIV,IPIV)-H(JPIV,JPIV))**2
      2+4.0*H(IPIV,JPIV)**2))
       COSINE=1.0/SQRT(1.0+TANG**2)
       SINE=TANG*COSINE
```

```
      HII=H(IPIV,IPIV)
      H(IPIV,IPIV)=COSINE**2*(HII+TANG*(2.*H(IPIV,JPIV)+TANG*H(JPIV,
     1JPIV)))
      H(JPIV,JPIV)=COSINE**2*(H(JPIV,JPIV)-TANG*(2.*H(IPIV,JPIV)
     1-TANG*HII))
      H(IPIV,JPIV)=0.
C
C      PSEUDO RANK THE EIGENVALUES
C      ADJUST SINE AND COS FOR COMPUTATION OF H(IK) AND U(IK)
      IF ( H(IPIV,IPIV) -  H(JPIV,JPIV)) 152,153,153
 152  HTEMP = H(IPIV,IPIV)
      H(IPIV,IPIV) = H(JPIV,JPIV)
      H(JPIV,JPIV) = HTEMP
C       RECOMPUTE SINE AND COS
      HTEMP = SIGN(1.0, -SINE) * COSINE
      COSINE = ABS(SINE)
      SINE = HTEMP
 153  CONTINUE
C
C     INSPECT THE IQS BETWEEN I+1 AND N-1 TO DETERMINE
C     WHETHER A NEW MAXIMUM VALUE SHOULD BE COMPUTED SINCE
C     THE PRESENT MAXIMUM IS IN THE I OR J ROW.
C
      DO 350 I=1,NMI1
      IF(I-IPIV)210,350,200
 200  IF(I-JPIV)210,350,210
 210  IF(IQ(I)-IPIV)230,240,230
 230  IF(IQ(I)-JPIV)350,240,350
 240  K=IQ(I)
 250  HTEMP=H(I,K)
      H(I,K)=0.
      IPL1=I+1
      X(I) =0.
C
C     SEARCH IN DEPLETED ROW FOR NEW MAXIMUM
C
      DO 320 J=IPL1,N
      IF ( X(I)- ABS( H(I,J)) ) 300,300,320
 300  X(I) = ABS(H(I,J))
      IQ(I)=J
 320  CONTINUE
      H(I,K)=HTEMP
 350  CONTINUE
C
      X(IPIV) =0.
      X(JPIV) =0.
C
C     CHANGE THE OTHER ELEMENTS OF H
C
      DO 530 I=1,N
C
      IF(I-IPIV)370,530,420
 370  HTEMP = H(I,IPIV)
      H(I,IPIV) = COSINE*HTEMP + SINE*H(I,JPIV)
      IF ( X(I) - ABS( H(I,IPIV)) )380,390,390
```

```
 380  X(I) = ABS(H(I,IPIV))
      IQ(I) = IPIV
 390  H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)
      IF ( X(I) - ABS( H(I,JPIV)) ) 400,530,530
 400  X(I) = ABS(H(I,JPIV))
      IQ(I) = JPIV
      GO TO 530
C
 420  IF(I-JPIV)430,530,480
 430  HTEMP = H(IPIV,I)
      H(IPIV,I) = COSINE*HTEMP + SINE*H(I,JPIV)
      IF ( X(IPIV) - ABS( H(IPIV,I)) ) 440,450,450
 440  X(IPIV) = ABS(H(IPIV,I))
      IQ(IPIV) = I
 450  H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)
      IF ( X(I) - ABS( H(I,JPIV)) ) 400,530,530
C
 480  HTEMP = H(IPIV,I)
      H(IPIV,I) = COSINE*HTEMP + SINE*H(JPIV,I)
      IF ( X(IPIV) - ABS( H(IPIV,I)) ) 490,500,500
 490  X(IPIV) = ABS(H(IPIV,I))
      IQ(IPIV) = I
 500  H(JPIV,I) = -SINE*HTEMP + COSINE*H(JPIV,I)
      IF ( X(JPIV) - ABS( H(JPIV,I)) ) 510,530,530
 510  X(JPIV) = ABS(H(JPIV,I))
      IQ(JPIV) = I
 530  CONTINUE
C
C     TEST FOR COMPUTATION OF EIGENVECTORS
C
      IF(IEGEN)40,540,40
 540  DO 550 I=1,N
      HTEMP=U(I,IPIV)
      U(I,IPIV)=COSINE*HTEMP+SINE*U(I,JPIV)
 550  U(I,JPIV)=-SINE*HTEMP+COSINE*U(I,JPIV)
      GO TO 40
 1000 CONTINUE
        WRITE(36,1001) NR
      IF(N.EQ.1) RETURN
 1001 FORMAT(1H0,I10)
C     THIS SECTION HAS BEEN ADDED SO AS TO ORDER EIGENVECTORS
C     ABSOLUTELY
      NM=N-1
      DO 740 J=1,NM
      JP=J+1
      DO 743 K=1,J
      IF (H(K,K)-H(JP,JP)) 741,743,743
  741 CONTINUE
      HH=H(K,K)
      H(K,K)=H(JP,JP)
      H(JP,JP)=HH
      DO 742 I=1,N
       X(I)=U(I,K)
      U(I,K)=U(I,JP)
      U(I,JP)=X(I)
```

```
742 CONTINUE
743 CONTINUE
740 CONTINUE
    RETURN
    END
```

3. Program to calculate energy levels and eigenvectors

```
C        THIS PROGRAM DIMENSIONS ARRAYS AND OPENS AND CLOSES
C       FILES FOR THE SUBROUTINE HAMLTN.
      DIMENSION S(43,43),F(43,43),Q(284),QQ(284),E(284),AS(284),
     1UT(284,24),JAY(284,25),EXTRA(43,43),OCC(43),IORB(43),IATOM(43),
     2QOLD(71),QNEW(71),QCORE(71),DIFF(71),
     3WP(8),WN(8),VP(8),VN(8),NAK(5),NORB(5)
      MAXB=22
      MORB=140
      MAXU=24
      JMAX=25
      NATOM=35
      NFUN=8
      KATM=4
      CALL OPCLS(0)
      TYPE 200
  200 FORMAT(' XX= ?')
      ACCEPT 201,XX
  201 FORMAT(F)
      TYPE 202,XX
  202 FORMAT(' XX='F)
      CALL HAMLTN(S,F,Q,QQ,E,AS,UT,JAY,EXTRA,OCC,QOLD,QNEW,
     1QCORE,DIFF,IORB,IATOM,WP,WN,VN,VP,NAK,NORB,MAXB,MORB,MAXU,JMAX,
     2NATOM,NFUN,KATM,XX)
      STOP
      END
      SUBROUTINE OPCLS(K)
      IF(K.EQ.1) GO TO 1
      OPEN(UNIT=20,DEVICE='DSK',FILE='UMAT35.DAT',DIRECTORY='4,270'
     1,DIALOG)
      OPEN(UNIT=23,DEVICE='DSK',FILE='QIN35.DAT',DIRECTORY='4,270'
     1,DIALOG)
      OPEN(UNIT=24,DEVICE='DSK',FILE='QOUT35.DAT',DIRECTORY='4,270'
     1,DIALOG)
      OPEN(UNIT=32,DEVICE='DSK',FILE='H2IN35.DAT',DIRECTORY='4,270'
     1,DIALOG)
      OPEN(UNIT=33,DEVICE='DSK',FILE='SGXN35.DAT',DIRECTORY='4,270'
     1,DIALOG)
      OPEN(UNIT=34,DEVICE='DSK',FILE='HGXN35.DAT',DIRECTORY='4,270'
     1,DIALOG)
      OPEN(UNIT=36,DEVICE='DSK',FILE='H4OT35.DAT',DIRECTORY='4,270',
     1DIALOG)
      OPEN(UNIT=42,MODE='BINARY',DEVICE='DSK',DIRECTORY='4,270',
     1FILE='SAMAT.DAT')
      RETURN
    1 CONTINUE
      CLOSE(UNIT=20)
      CLOSE(UNIT=23)
      CLOSE(UNIT=24)
      CLOSE(UNIT=32)
      CLOSE(UNIT=33)
      CLOSE(UNIT=34)
      CLOSE(UNIT=36)
      CLOSE(UNIT=42,MODE='BINARY',DEVICE='DSK',DIRECTORY='4,270',
     1FILE='SAMAT.DAT')
      CLOSE(UNIT=41,DEVICE='DSK',MODE='BINARY',ACCESS='RANDOM',
```

```
     1ASSOCIATE VARIABLE=NREC,RECORD SIZE=2500,FILE='FOR41.DAT',
     2DISPOSE='DELETE')
      RETURN
      END
C
C
C
C       PROGRAM OBTAINED FROM D. FRANCESCHETTI, OCTOBER, 1977
C       MODIFIED BY D. MILLER AND C. SWARTS
C
C        PROGRAM HAMILTON
C        CONSTRUCTS EXTENDED HUCKEL HAMILTONIAN AND SOLVES SECULAR
C        EQUATION
      SUBROUTINE HAMLTN (S,F,Q,QQ,E,AS,UT,JAY,EXTRA,OCC,QOLD,QNEW,
     1QCORE,DIFF,IORB,IATOM,WP,WN,VN,VP,NAK,NORB,MAXB,NSO,MAXU,JMAX,
     2NATOM,NFUN,KATM,XX)
      DIMENSION S(MAXB,MAXB),F(MAXB,MAXB),Q(NSO),QQ(NSO),E(NSO),
     1AS(NSO),UT(NSO,MAXU),JAY(NSO,JMAX),EXTRA(MAXB,MAXB),OCC(MAXB),
     2QOLD(NATOM),QNEW(NATOM),QCORE(NATOM),DIFF(NATOM),IORB(MAXB),
     3IATOM(MAXB),WP(NFUN),WN(NFUN),VN(NFUN),VP(NFUN),NAK(KATM),
     4NORB(KATM)
      ETOTAL=0
      NDIM=MAXB
      READ(32,77) NSO,NATOM,NFUN,KATM,IX
      WRITE(36,77) NSO,NATOM,NFUN,KATM,IX
      READ(32,77) (NAK(I),NORB(I),I=1,KATM)
      WRITE(36,77) (NAK(I),NORB(I),I=1,KATM)
      READ(32,510) AK1,AK2,AK3,AK4,AK5,AK6
      WRITE(36,510) AK1,AK2,AK3,AK4,AK5,AK6
  510 FORMAT(6F10.6)
      READ(20,75) JMAX,MAXU
      WRITE(36,77) JMAX,MAXU
   77 FORMAT(8I5)
   78 FORMAT(F10.6)
      READ (20,65) ((UT(I,J),J=1,MAXU),I=1,NSO)
      READ (20,75) ((JAY(I,J),J=1,JMAX),I=1,NSO)
   75 FORMAT(9I8)
   65 FORMAT (8E14.7)
        READ (32,8)((WP(I),VP(I)),I=1,NFUN)
        WRITE(36,8) ((WP(I),VP(I)),I=1,NFUN)
        READ (32,8) ((WN(I),VN(I)),I=1,NFUN)
        WRITE(36,8) ((WN(I),VN(I)),I=1,NFUN)
    8   FORMAT(8F10.6)
      DO 99 I=5,6
      J=I+2
      WN(I)=XX*WN(I)+(1.-XX)*WN(J)
      WP(I)=XX*WP(I)+(1.-XX)*WP(J)
      VN(I)=XX*VN(I)+(1.-XX)*VN(J)
   99 VP(I)=XX*VP(I)+(1.-XX)*VP(J)
      READ (24,4) (QOLD(I),I=1,NATOM)
4     FORMAT(8F10.6)
      NOLD=0
      REWIND 24
      DO 12 I=1,NSO
   12 Q(I)=0.
```

```
      L=1
      READ (32,2)IT
      WRITE(36,2) IT
      DO 5 ITIMES=1,IT
      READ (32,2)N,KA
    2 FORMAT(3I5)
        READ (32,222) (OCC(I),I=1,N)
  222 FORMAT(16F5.2)
        READ (32,322) (IORB(I),I=1,N)
        READ (32,322) (IATOM(I),I=1,N)
  322 FORMAT(40I2)
      READ (33,1) ((S(I,J),J=1,N),I=1,N)
        DO 333 I=1,N
        DO 333 J=1,N
  333 EXTRA(I,J)=S(I,J)
        DO 223 I=1,N
        QI=QOLD(IATOM(I))
        IF(QI) 224,225,225
  224 FX=WN(IORB(I))*QI+VN(IORB(I))
        GO TO 226
  225 FX=WP(IORB(I))*QI+VP(IORB(I))
  226 CONTINUE
  223 F(I,I)=FX
C     AT THIS POINT THE DIAGONAL ELEMENTS OF F ARE THE VALENCE
C     STATE IONIZATION POTENTIALS OF THE ATOMIC ORBITALS FROM
C     WHICH THE CORRESPONDING SYMMETRY ORBITAL HAS BEEN CONSTRUCTED.
C     WE NOW CONSTRUCT THE OFF-DIAGONAL ELEMENTS OF THE HAMILTONIAN.
        NM=N-1
        DO 227 I=1,NM
        IP=I+1
        DO 227 J=IP,N
      IIO=(IORB(I)+IORB(J))/2
      FIO=FLOAT(IORB(I)+IORB(J))/2.-.1
      IF(IORB(I).LE.2.AND.IORB(J).GT.2) GO TO 500
      IF(IORB(I).GT.2.AND.IORB(J).LE.2) GO TO 500
      IF(IIO.LT.FIO) GO TO 501
      AK=AK1
      GO TO 502
  501 AK=AK2
      GO TO 502
  500 IF(IORB(I).EQ.2.OR.IORB(J).EQ.2) GO TO 503
      IF(IIO.LT.FIO) GO TO 504
      AK=AK3
      GO TO 502
  504 AK=AK4
      GO TO 502
  503 IF(IIO.LT.FIO) GO TO 505
      AK=AK5
      GO TO 502
  505 AK=AK6
  502 CONTINUE
        F(I,J)=.5*(F(I,I)+F(J,J))*S(I,J)*AK
  227 CONTINUE
        DO 229 I=1,NM
        IP=I+1
```

```
      DO 229 J=IP,N
      IF (JAY(NOLD+I,1)-JAY(NOLD+J,1)) 230,232,230
  232 SUB=0
      K1MAX=JAY(NOLD+I,JMAX)
      K2MAX=JAY(NOLD+J,JMAX)
      DO 233 K1=1,K1MAX
      DO 233 K2=1,K2MAX
      IF (JAY(NOLD+I,K1)-JAY(NOLD+J,K2)) 234,235,234
  235 SUB=SUB+UT(NOLD+I,K1)*UT(NOLD+J,K2)
  234 CONTINUE
  233 CONTINUE
      AKM=1.-AK
      F(I,J)=F(I,J)+SUB*AKM*0.5*(F(I,I)+F(J,J))
  230 CONTINUE
  229 CONTINUE
C     FILL IN LOWER OFF DIAGONAL ELEMENTS
      DO 236 I=1,NM
      IP=I+1
      DO 236 J=IP,N
  236 F(J,I)=F(I,J)
C     NOW FIX UP THE DIAGONAL ELEMENTS
      AK=AK1
      AKM=1.-AK
      DO 237 I=1,N
      SUB=0
      KMAX=JAY(NOLD+I,JMAX)
      DO 238 K=1,KMAX
  238 SUB=SUB+UT(NOLD+I,K)**2
  237 F(I,I)=F(I,I)*(AK*S(I,I)+AKM*SUB)
    1 FORMAT(8E14.7)
      CALL CHARA(S,F,N,O,KA,NDIM,Q,QQ,AS,UT,MAXU,JAY,JMAX,EXTRA,NOLD,
     1NSO,ETOTAL,OCC,IX)
      DO 3 I=1,N
      E(L)=AS(I)
    3 L=L+1
      NOLD=NOLD+N
    5 CONTINUE
      L=L-1
      DO 7 I=2,L
      DO 7 J=I,L
      IF(E(I-1)-E(J)) 6,7,7
    6 EE=E(J)
      E(J)=E(I-1)
      E(I-1)=EE
    7 CONTINUE
      WRITE(36,88) ((I,E(I)),I=1,L)
   88 FORMAT(5(I5,F15.4))
      EK=ETOTAL*23.07
      TYPE 10, ETOTAL, EK
      WRITE(36,10) ,ETOTAL,EK
   10 FORMAT(2F20.4)
      IF(IX) 86,87,86
   86 CALL OPCLS(1)
      CALL EXIT
   87 CONTINUE
```

```
      READ (32,32) (QCORE(I),I=1,NATOM)
   32 FORMAT(16F5.3)
      DO 20 I=1,NATOM
   20 QQ(I)=0.
      IFIND=0
      IATM=0
      DO 13 I=1,KATM
      IF(NAK(I).LE.0) GO TO 13
      DO 14 J=1,NAK(I)
      DO 15 K=1,NORB(I)
   15 QQ(IATM+J)=QQ(IATM+J)+Q(IFIND+K)
   14 IFIND=IFIND+NORB(I)
   13 IATM=IATM+NAK(I)
      WRITE(36,21)
   21 FORMAT (23HONET ATOMIC POPULATIONS)
      DO 23 I=1,NATOM
      QQ(I)=QCORE(I)-QQ(I)
      DIFF(I)=QQ(I)-QOLD(I)
   23 QNEW(I)=(10.*QOLD(I)+QQ(I))/11.
      WRITE(36,33)
        TYPE 33
   33 FORMAT (41HOINITIAL Q  NEW Q     CHANGE IN Q TRIAL Q   )
      SUMSQ=0.
      DO 35 I=1,NATOM
      WRITE(36,34) QOLD(I),QQ(I),DIFF(I),QNEW(I)
   34 FORMAT(1H ,4F10.5)
   35 SUMSQ=SUMSQ+DIFF(I)**2
      SUMSQ=SQRT(SUMSQ/(FLOAT(NATOM-1)))
      WRITE(36,36)  SUMSQ
        TYPE 36, SUMSQ
      WRITE (24,4) (QNEW(I),I=1,NATOM)
      TYPE 4, (QNEW(I),I=1,NATOM)
   36 FORMAT  (20HOSTANDARD DEVIATION=   ,F10.6)
   22 FORMAT (1H0, 5F10.5)
      CALL OPCLS(1)
      CALL EXIT
      END
      SUBROUTINE CHARA (S,HB,N,IDEA,KA,NDIM,Q,QQ,AS,UT,MAXU,JAY,JMAX,
     1EXTRA,NOLD,NSO,ETOTAL,OCC,IX)
      DIMENSION S(NDIM,NDIM),HB(NDIM,NDIM),Q(NSO),QQ(NSO)
      DIMENSION AS(NDIM),UT(NSO,MAXU),JAY(NSO,JMAX),EXTRA(NDIM,NDIM),
     1OCC(NDIM)
C     THIS SUBROUTINE CALLS THE MATRIX DIAGONALIZATION ROUTINE  EIGEN
C     CALLS THE POPULATION ANALYSIS SUBROUTINE - MULLIK
      WRITE(36,44)
   44 FORMAT(1H0,60X,18HHAMILTONIAN MATRIX)
      CALL PEGLEG(HB,N,NDIM)
      CALL EIGEN(S,HB,N,NDIM,AS,IX)
   13 FORMAT(1H0,18H ORBITAL CHARGES          )
  404 FORMAT(6F12.8)
      IF(IDEA-2) 401,402,401
  402 KAK=N-KA+1
      WRITE (24,404)((HB(I,J),I=1,N),J=KAK,N)
  401 CONTINUE
      IF(IX.NE.0) GO TO 491
```

```
      CALL MULLIK (UT,MAXU,JAY,JMAX,EXTRA,HB,Q,AS,NOLD,NSO,NDIM,N,KA,
     1ETOTAL,OCC)
 1073 CONTINUE
      IF(KA) 715,714,715
  714 RETURN
  715 CONTINUE
      WRITE (36,13)
      WRITE (36,11)(Q(I),I=1,NSO)
      IF(IDEA-2) 491,492,491
  492 WRITE (24,404)(Q(I),I=1,NSO)
  491 CONTINUE
   11 FORMAT (15F8.4)
      RETURN
      END
      SUBROUTINE MULLIK (UT,MAXU,JAY,JMAX,EXTRA,C,Q,AS,NOLD,NSO,NDIM
     1,N,KA,ETOTAL,OCC)
      DIMENSION UT(NSO,MAXU),JAY(NSO,JMAX),EXTRA(NDIM,NDIM),Q(NSO)
     1,C(NDIM,NDIM),AS(NDIM),OCC(NDIM)
        I=NSO
      NLOW=N-KA+1
      CALL MMULT(EXTRA,C,N,NDIM)
      DO 1 J=1,N
      DO 1 J2=1,N
        N1=NOLD+J
        N2=NOLD+J2
      K1MAX=JAY(N1,JMAX)
      K2MAX=JAY(N2,JMAX)
      DO 1 K1=1,K1MAX
      DO 1 K2=1,K2MAX
      JARG=JAY(N1,K1)
      J2ARG=JAY(N2,K2)
        IF(JARG-J2ARG) 1,3,1
    3 PROD=UT(N1,K1)*UT(N2,K2)
      IF(JARG.NE.J2ARG) GO TO 1
      DO 2 I=NLOW,N
        Q(JARG)=Q(JARG)+OCC(I)*C(J,I)*EXTRA(J2,I)*PROD
    2 CONTINUE
    1 CONTINUE
      DO 792 I=NLOW,N
        ETOTAL=ETOTAL+OCC(I)*AS(I)
  792 CONTINUE
      RETURN
      END
      SUBROUTINE EIGEN(SA,C,N,NDIM,AS,IX)
      DIMENSION SA(NDIM,NDIM),C(NDIM,NDIM),AS(NDIM)
C     SAVE C MATRIX ON UNIT 11
C      REWIND 41
       OPEN(UNIT=41,MODE='BINARY',ACCESS='RANDOM',ASSOCIATEVARIABLE
     1=NREC,RECORDSIZE=2500,DEVICE='DSK',FILE='FOR41.DAT')

      WRITE(41#1)((C(I,J),J=1,N),I=1,N)
C      THIS SUBROUTINE SOLVES THE MATRIX EQUATION (H-ES)C=0   USING
C      HDIAG
       READ(34,65) ((C(I,J),J=1,N),I=1,N)
   65 FORMAT(8E14.7)
```

```
        DO 901 I=1,N
  901 READ (34,65) SA(I,I)
      DO 506 I=1,N
      SA(I,I)=1.0/SQRT(SA(I,I))
  506 CONTINUE
C     WRITE U**T
      WRITE(41#2)((C(I,J),I=1,N),J=1,N)
C      BACKSPACE 41
C     FORM MATRIX U(I,K)*OM(K,K)
      DO 509 K=1,N
      OM = SA(K,K)
      DO 509 I=1, N
  509 SA(I,K) = OM*C(I,K)
C     READ U**T
      READ(41#2)((C(I,J),J=1,N),I=1,N)
C     FORM W = U(I,K)*OM(K,K)*U**T
      CALL MMULT(SA,C,N,NDIM)
C     SAVE W
C      BACKSPACE 41
      WRITE(41#2)((SA(I,J),J=1,N),I=1,N)
C      REWIND 41
C     READ ORIGINAL C AND FORM C*W
      READ(41#1)((C(I,J),J=1,N),I=1,N)
      CALL MMULT(C,SA,N,NDIM)
C     FORM W*C*W = SA
      CALL MMULT(SA,C,N,NDIM)
      CALL HDIAG(SA,N,IX,C,NR,NDIM)
      WRITE (36,1961)
        TYPE 1961
      WRITE (36,820)((I, SA(I,I)),I=1,N )
        TYPE 820, (I,SA(I,I),I=1,N)
      DO 1 I=1,N
    1 AS(I)=SA(I,I)
      IF(IX.NE.0)RETURN
      REWIND 42
      WRITE(42)((SA(I,J),J=1,N),I=1,N)
      READ(41#2)((SA(I,J),J=1,N),I=1,N)
C     FORM W*C
      CALL MMULT(SA,C,N,NDIM)
      DO 519 I=1, N
      DO 519 J=1, N
  519 C(I,J) = SA(I,J)
      REWIND 42
      READ(42)((SA(I,J),J=1,N),I=1,N)
 1961 FORMAT(1H0,55X,25H ENERGY LEVELS (EV)                    )
  820 FORMAT( 1H0, 51X,2HE(I3,3H) =F12.4)
  822 FORMAT(1H0,50X,12HALL IS WELL      //)
      WRITE (36,3001)
 3001 FORMAT(1H0,60X,15HWAVE FUNCTIONS                    )
      CALL PEGLEG(C,N,NDIM)
C     THE WAVE FUNCTIONS ARE PRINTED OUT IN A MATRIX   THE COLUMNS
C     OF WHICH ARE THE EIGENVECTORS BELONGING TO THE EIGENVALUE WITH
C     THE NUMBER OF THE COLUMN.
      RETURN
      END
```

```
      SUBROUTINE MMULT(A,B,N,NDIM)
      DIMENSION A(NDIM,NDIM), B(NDIM,NDIM), X(150)
C     ROUTINE FORMS THE MATRIX PRODUCT A = A*B
        I=NDIM
      DO 1 I=1, N
      DO 2 J=1, N
      X(J) =0.
      DO 2 K=1,N
    2 X(J) = X(J)+A(I,K)*B(K,J)
      DO 1 L=1, N
    1 A(I,L) = X(L)
      RETURN
      END
```

REFERENCES

1. D. J. Wolford, B. G. Streetman, R. J. Nelson, and N. Holonyak, Jr., Solid State Commun. 19, 741(1976).

2. W. Y. Hsu, J. D. Dow, D. J. Wolford, and B. G. Streetman, Phys. Rev. B 16, 1597 (1977).

3. A review of the current status of the defect problem may be found in S. T. Pantelides, IBM Research Report, RC 6952 (#29802), 1978; and to be published.

4. L. Eisenstein and D. R. Franceschetti, Chem. Phys. Lett. 50, 167 (1977).

5. R. P. Messmer and G. D. Watkins, Phys. Rev. B 7, 2568 (1973).

6. G. D. Watkins and R. P. Messmer, in Computational Methods for Large Molecules and Localized States in Solids, eds. F. Herman, A. D. McLean, and R. K. Nesbet (Plenum Press, New York, 1973), p. 133.

7. F. P. Larkins, J. Phys. C. 4, 3065 (1971); and J. Phys. C 4, 3077 (1971).

8. c.f. T. L. Gilbert, in Sigma Molecular Orbital Theory, ed. O. Sinanoglu and K. B. Wiberg (Yale University Press, New Haven, 1970), p. 249.

9. R. P. Messmer, Chem. Phys. Lett. 11, 589 (1971).

10. T. F. Lee and T. C. McGill, J. Phys. C 6, 3438 (1973).

11. E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables 14, 177 (1974).

12. C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

13. M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).

14. R. S. Mulliken, J. Chem. Phys. 23, 1841 (1955).

15. M. Tinkham, Group Theory and Quantum Mechanics, (McGraw-Hill, New York, 1964).

VITA

Donald Lynn Miller was born in [redacted] He attended Our Lady of the Ozarks High School, Carthage, Missouri, from which he graduated in May, 1969. He then entered the University of Missouri, Columbia, Missouri, from which he graduated in June, 1973. His graduate work was done at the University of Illinois, Urbana, Illinois, first as a National Science Foundation Graduate Fellow, and later as a H. J. Diffenbaugh Fellow. He received his masters degree in June 1974. He is a member of Phi Beta Kappa and the American Physical Society.