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AB INITIO METHODS FOR ELECTRON-MOLECULE COLLISIONS

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" For all we know and all we guess, we mutually impart" - Iolanthe

INTRODUCTION

If we take the strict definition of "*ab initio*"- from first principles, our review is at an end since no methods currently exist for treating the entire electron-molecule collisional process exactly. However, if we relax this definition to include those techniques that give the most accurate treatment of the various interactions, then we can discuss numerous prescriptions. In this sense, "*ab initio*" takes on a time-dependent character. The earliest treatments had to rely upon crude models for the interactions and scattering process. By the mid-1960's with the advent of electronic computers, the static or direct electrostatic interaction could be treated accurately while in the next decade, full treatments of the nonlocal exchange effects, at least for scattering from the ground state, began to be succesfully applied. The last few years have witnessed a vast expansion of our ability to treat electron-scattering processes with correlation and multi-channel coupling effects being included for a variety of small molecular targets. These new methods allow us to handle such mechanisms as polarization, channel and resonance interference, and autoionzation in a systematic and consistent fashion.

In this review, we shall concentrate on the recent advances in treating the *electronic* aspect of the electron-molecule intreaction and leave to other articles the description of the rotational and vibrational motions. We shall focus on those *methods which give the most complete treatment of the direct*, *exchange, and correlation effects*. Such full treatments are generally necessary at energies below a few Rydbergs($\approx$ 60eV). This choice unfortunately obliges us to omit those active and vital areas devoted to the development of model potentials and approximate scattering formaulations. The *ab initio* and model approaches complement each other and are both extremely important to the full explication of the electron-scattering process. Due to the rapid developments of recent years, we must however concentrate on the approaches that provide the fullest treatment.

That all three effects mentioned above are important in low-energy electron-molecule scattering is demonstrated in Fig.1 in which we compare calculations and experimental results for the total elastic cross section for electron collisions with molecular hydrogen. Even at an energy of 1 Ry., using only the static(S) interaction leads to errors of over thirty percent. The situation is improved by an exact treatment of exchange(SE). However, the static-exchange calculation does not reproduce the maximum in the cross section near 4 eV nor the very low-energy behavior. These features are obtained only by introducing polarization-correlation effects through an effective optical potential. The full interaction is needed to properly represent the weak resonance in the sigma-ungerade channel. As the figure demonstrates, new theoretical and computational techniques are now available that can treat the full range of the electron-scattering process.

The ability to treat all aspects of electron scattering on an equal footing allows us to probe more deeply the basic collisional processes and possibly to discover new mechanisms not properly represented by models. Certainly the development of tunable light sources such as the synchrotron(Dehmer et. al.,1986), which produces high-resolution spectra over wide energy ranges, place a heavy burden on the theoretical formaulations since intricate details must now be reproduced and explained. Before delving into the arcane lore of the methods, we present an example of the types of processes that can be explored with these more elaborate treatments. We consider the seemingly very simple event of electron scattering from the hydrogen molecular ion below the first excitation threshold. While only elastic scattering is possible, we encounter series of Feshbach resonances, which result from the temporary trapping of the incident electron in doubly-excited states of molecular hydrogen. These compound or autoionizing states must eventually decay to the continuum. The resonance is characterized by this decay time,τ, or its related width($1/\tau$). The series converge on the various excited states of the target ion. For example, if we consider scattering in total symmetry $^3\Pi_u$, then we have a set of autoionizing states of the form $1\sigma_u n\pi_g$ converging on the $1\sigma_u$ threshold and $1\pi_u^{+} n\sigma_u$ on $1\pi_u$ For certain conditions, these two series may overlap. We investigate this effect in Fig.2 in which we follow the resonant width of the two lowest compound states as a function of the separation of the two nuclei,R. We note that at values of R around 1. bohr, we encounter a strong coupling between the series leading to rather dramatic changes in the widths. To properly describe such interference requires at least a three-state close-coupling calculation. These effects may play important roles in such processes as dissociative photoionization and dielectronic recombination.

The situation at present for <u>ab initio</u> methods is indeed propitious with many techniques of equal sophistication available. Therefore, important cross-comparisons are possible in order to determine the range and validity of the various approaches. The length of this review precludes a comprehensive treatment of each technique. Instead, we shall concentrate on the general procedures for solving the electron scattering problem, illustrating these points with examples from the various methods. We begin with a brief description of the basic electron-molecule scattering formulation. We then present several strategies, common to most of the methods, for reducing the formulation to a more tractable form. We follow with a short summary of the general methods of solution and conclude by comparing the results of several methods and reviewing the general status of the field.

FORMULATION

> "And we are right, I think you'll say,
> to argue in this kind of way" - Mikado

Since the details of the general formulation for the scattering of an electron by an n-electron molecule, containing N nuclei, are clearly presented in other reviews(Lane,1980;Norcross and Collins,1982;Morrison,1983;Bucklet et al.,1984), we give only a brief outline of the basic precepts. We sacrifice rigorous formalism for a general, schematic view of the guiding principles behind the various methods. Therefore, at times, we shall mix our "scattering metaphors" in order to evoke a broad view of specific procedures. We describe the collisional process in terms of the solution to a Schrodinger equation of the form:

$$H\,\psi(\vec{r},\vec{X}) = E\,\psi(\vec{r},\vec{X}) \;, \tag{1}$$

where

$$H = T + V + H_{mol} \;, \tag{2a}$$

with T, the kinetic energy of the incident electron; V, the interaction of the free electron with the molecular electrons and nuclei

$$V = -\sum_{\gamma=1}^{N} Z_\gamma\,(\vec{r}-\vec{X}_\gamma)^{-1} + \sum_{i=1}^{n}(\vec{r}-\vec{x}_i)^{-1} \;; \tag{2b}$$

H_{mol}, the hamiltonian for the molecular target; and $\vec{r}$, the position of the continuum electron. We let $\vec{X}$ represent the coordinates of both the target electrons $\vec{x}_i (i=1,n)$ and the nuclei $\vec{X}_\gamma (\gamma=1,N)$, and refer all positions to an axis fixed in space. The molecular hamiltonian describes not only the interactions among the electrons and nuclei but also their respective motion. We convert this many-body problem to an effective single-particle one by expanding the total system wavefunction, ψ, in terms of a complete set of target states as

$$\psi(\vec{r},\vec{X}) = \Sigma_\alpha\, A[F_\alpha(\vec{r})\,\phi_\alpha(\vec{X})] \;, \tag{3a}$$

such that

$$H_{mol}\,\phi_\alpha(\vec{X}) = \epsilon_\alpha\,\phi_\alpha(\vec{X}) \;, \tag{3b}$$

where A is the antisymmetry operator. Inserting (3) into (1), multiplying through by the conjugate of a representative member, and integrating over all target coordinates, we obtain the following set of coupled integrodifferential equations(IDE's):

$$H_\alpha\,F_\alpha(\vec{r}) = \sum_\beta Z_{\alpha\beta}(\vec{r}) \;, \tag{4a}$$

where

$$H_\alpha = [\vec{\nabla}^2 + k_\alpha^2] ,$$

$$Z_{\alpha\beta}(\vec{r}) = \int K_{\alpha\beta}(\vec{r}|\vec{r}_1)\, F_\beta(\vec{r}_1)\, d\vec{r}_1 , \tag{4b}$$

$$K_{\alpha\beta}(\vec{r}|\vec{r}_1) = V_{\alpha\beta}(\vec{r}_1)\delta(\vec{r} - \vec{r}_1) + W_{\alpha\beta}(\vec{r}|\vec{r}_1) , \tag{4c}$$

with k_α^2 given by $2(E - \epsilon_\alpha)$. The direct electrostatic interaction, $V_{\alpha\beta}$, is local and given by an integral involving the interaction V and two target states, $\langle\alpha|V|\beta\rangle$. The exchange interaction is schematically represented by $W_{\alpha\beta}$, which is a complicated nonlocal term that arises from the constraints imposed on the solution by the Pauli exclusion principle. We extract the collisional information, such as the reactance(K), transition(T), or scattering(S) matrices from which the cross sections are determined, by matching the solutions F to their proper asymptotic forms.

We also employ an equivalent form of (4) by converting to a set of coupled integral equations(IE's) by introducing a Green's function. In the case of the free-particle Green's function, we have

$$F_\alpha(\vec{r}) = F_\alpha^{\,o}(\vec{r}) + \sum_\beta \int G_\alpha^o(\vec{r}|\vec{r}_2)\, Z_{\alpha\beta}(\vec{r}_2)\, d\vec{r}_2 , \tag{5a}$$

where

$$H_\alpha F_\alpha^o(\vec{r}) = 0 \tag{5b}$$

and

$$H_\alpha G_\alpha^o (\vec{r}|\, \vec{r}_1) = \delta(\vec{r} - \vec{r}_1) . \tag{5c}$$

Equation (5) simply gives the coordinate-space respresentation of the standard Lippmann-Schwinger(LS) equation for the scattering solution F. In many cases, the IE formaulation provides a more stable framework from which to instigate a numerical solution. We can derive similar IE's for other scattering quantities such as the T-matrix. Im terms of symbolic-operator notation, we write these LS equations in the compact form(Taylor, 1972)-

$$\psi = \psi^o + G_o^+ V \psi \tag{5d}$$

$$T = V + V G_o^+ T \tag{5e}$$

where G_o^+ represents the out-going free-particle Green's function and T, the transition matrix operator. Despite our efforts, we still have a rather formidable "beastie" to conquer. To aid in this conquest, we devise several general strategies for further reducing the complications with little loss of accuracy.

STRATEGIES

"In short when I've a smattering of elemental strategy"- Pirates of Penzance

In (4), we have a complicated set of IDE's, whose coupling term is both nonlocal and energy dependent. In order to effect a solution, we hatch a variety of strategies, common to most of the principal methods, to make the solution more tractable.

S1: Adiabatic-nuclei approximation

The quantities in (4) all depend on the orientation and separation of the molecular nuclei,$R=(\vec{X}_\gamma)$. Since we are primarily concerned with the electronic interactions, we shall invoke the adiabatic-nuclei(AN) approximation(Temkin and Vasavada,1967;Hara,1967;Morrison;1987) by which the motion of the nuclei is assumed to be slow compared to that of the electrons. In this case, the molecular electrons have time to readjust to the new nuclear positions, and the electron-molecule collision may be treated in a sudden approximation with the nuclei frozen at a given value of R. In this case we can fix R and solve (4) for the scattering solutions F. By repeating this prescription at different values of R, we obtain a parameteric dependence of the collisional information. Quantities such as rotational- and vibrational-excitation cross sections are then found by averaging the R-dependendent scattering amplitudes over the appropriate eigenfunctions. For purposes of future discussions, we assume an implicit R dependence in the scattering wavefunction, and since the molecule is fixed in space, we refer all quantities to the body frame system centered on the molecule(z-axis along a major line of symmetry such as the internuclear axis in a diatomic). The AN approximation has a fairly wide range of validity but encounters problems when the colliding electron remains in the vicinity of the molecule for times comparable to the rotational or vibrational period(Morrison,1987;Jung et al.,1987). This condition arises for resonances in which a trapping occurs near the target, for energies close to threshold where the velocity of the incident electron is very low, and for encounters in very long-ranged potentials. The AN approximation can be relaxed by directly introducing approximations to the nonadiabatic effects(Schneider et al.,1979) into (4), by using a vibrational close-coupling prescription(Morrison and Saha,1986) or by utilizing some form of the frame transformation(Chang and Fano,1972;Norcross and Collins,1982).

S2: Spatial Dichotomy

The nonlocal terms in (4) present the greatest challenge to obtaining a solution. However, these terms are generally quite limited in range. Therefore, a useful stategy is to divide space into regions, based on the strength and nature of the interaction. One procedure for effecting this division is to impose arbitrary boundary conditions on the solution at some surface,Σ. For example, we might require a particular choice for the log-derivative -

$$\frac{1}{\psi}\,\frac{\partial(\psi)}{\partial n} = b\ , \tag{6a}$$

where $\partial/\partial n$ represents the surface-normal derivative. In the inner region, where all interactions are important, we solve the full Schrodinger equation of the form:

$$(H_b - E)\,|\psi) = L_b\,|\psi)\ , \tag{6b}$$

where

$$H_b = H + L_b . \tag{6c}$$

The standard hamiltonian, H, is given by (2a), and the Bloch(1957) operator L_b guarantees that the solution to (6b) satisfies the proper boundary conditions at Σ. For a spherically symmetric case with b=0, we have

$$L_b = \delta(r - a) \frac{d}{dr} , \tag{6d}$$

where r=a defines the boundary. The rounded brackets signify that the solution and all operations such as integrals are restricted to the volume within the surface.. In the outer region, where the interaction terms become local and usually expressable as inverse powers of r, we employ standard asymptotic expansion(Noble and Nesbet,1984) or propagation schemes(Light and Walker,1976). We obtain a great advantage by this zoning of space. In the restricted inner region($r \le 10 - 20$ bohr), the full force of the ab initio techniques can be brought to bear while in the outer region, where the interactions are much simpler, less sophisticated techniques can be employed. We could also impose an implicit dichotomy by using basis functions that properly represent the wavefunctions in each region.

S3: P-Q Division

"He minds his P's and Q's, and keeps himself respectable"-Utopia,Ltd.

In many applications, we are only interested in the scattering information for a few of the states in expansion (3). In this case, we employ the standard Feshbach(1958) formalism in order to isolate these states. We use an expansion of the form:

$$\psi(\vec{r},\vec{x}) = (P + Q)\, \psi(\vec{r},\vec{x}) , \tag{7}$$

where the projection operators are defined as

$$P\,\psi = \sum_{\alpha=1}^{m} | A(F_\alpha(\vec{r})\, \phi_\alpha(\vec{x}))> < A(F_\alpha(\vec{r})\, \phi_\alpha(\vec{x}))| \psi > \tag{8a}$$

$$Q\,\psi = \sum d_c \,|\, \chi_c(\vec{r},\vec{x}) > < \chi_c(\vec{r},\vec{x}) \,|\, \psi > . \tag{8b}$$

This choice of projection operators is not unique; some prescriptions define P and Q in terms of only the n-electron target functions. In making this separation, we usually enforce the strong orthogonality constraint by which the orbitals that compose χ and ψ are assumed to be orthogonal to all continuum solutions,F. The summation in the first term ranges over a limited number of target states(m), usually those for which we directly seek information. The second term, which consists of n+1 electron functions, is added for completeness. These "correlation" functions, χ, can be used to relax the orthogonality constraints and to represent other correlation effects not included in the first term.

By substituting this expression into (1) and multiplying through in an operator sense by P and Q separately, we derive the following two equations:

$$H_{PP}\,\psi_P + H_{PQ}\,\psi_Q = E\,\psi_P \tag{9a}$$

$$H_{QP}\,\psi_P + H_{QQ}\,\psi_Q = E\,\psi_Q \tag{9b}$$

where $H_{XY} = \langle X|H|Y\rangle$ and $\psi_X = \langle X|\psi\rangle$. Solving (9b) for ψ_Q and substituting the result into (9a), we obtain the following equation for the P-space function:

$$[\,(H_{PP} - E) + V_{opt}\,]\,\psi_P = 0 \quad , \tag{10a}$$

where the optical potential is given by

$$V_{opt} = H_{PQ}\,(H_{QQ} - E)^{-1}\,H_{QP} \quad . \tag{10b}$$

The derivation so far is merely a formal rearangement of the original Schrodinger eqaution. However, this form in terms of the P-space solution has many advantages. For example, we may be able to make approximations to (10b) that allow us to calculate the optical potential directly. In this case, we are left with only having to solve the P-space equations over a small set of functions.

To utilize this division, we must effectively balance the size of the P and Q spaces. In the traditional close-coupling(CC) approach, we set the coefficients of the correlation functions to zero and add target functions to the first term until convergengence is reached. This convergence in terms of target functions can be quite slow. In some methods this problem is rectified by adding a few psuedostates directly to the first expansion. These pseudostates are constructed so as to approximate the effects of those states omitted from the original expansion. In other approaches the P-space is kept small and the Q-space expanded, usually with eigenfunctions from a configuration-interaction(CI) calculation on the n+1 system.

S4: Separable expansions

The optical potential, which contains exchange and correlation effects, is a complicated nonlocal, energy-dependent expression. We can greatly simplify its form by making a separable expansion in terms of a discrete set of basis functions$\{\chi_\gamma\}$:

$$U_{opt}(\vec{r}\,|\,\vec{r}_1) = \sum_\alpha \sum_\beta \chi_\alpha(\vec{r})\;U_{\alpha\beta}\;\chi_\beta(\vec{r}_1) \tag{11a}$$

where

$$U_{\alpha\beta} = \langle\,\alpha\,|\,U_{opt}\,|\,\beta\,\rangle \quad , \tag{11b}$$

and $\langle\alpha|\beta\rangle = \delta_{\alpha\beta}$. Such separable expansions have a wide variety of apllications in electron-molecule scattering. For example, a modified form of (11) applied to the LS equations can be used to ensure equivalence to variational procedures such as the Schwinger. In addition, their use in numerical evaluations of exchange and correlation terms can greatly reduce computaional times with only minor loss of accuracy(Collins and Schneider,1986)

METHODS OF SOLUTION: OVERVIEW

"Existence was slow and we wanted variety" - Gondoliers

In this section, we present a brief overview of the plethora of techniques that have evolved to treat electron-molecule collisions and illustrate each general area with one of the more heavily utilized methods. We should probably view it in the spirit of a patter song from a Gilbert and Sullivan operetta giving a rapid listing with meager explanation in order to evoke a sense of the vast effort that has occupied the field for several decades. A more detailed accounting of methods and practioners is given in the Appendix and in reference 4. This tact frees us from an excrescence of citations in the body of this section. We shall only use references to differentiate methods within a specific area or to introduce additional material not covered in the Appendix. Comprehensive reviews of the R-matrix, Schwinger variational, and linear algebraic methods are scheduled to appear in a future issue of Computer Physics Reports. Tradition dicates the division of the methods of solution into two distinct categories: 1) numerical and 2) square integrable. We shall follow this convention although the boundaries between these approaches has greatly blurred since most of the current techniques employ both prescriptions.

Numerical Methods

In most of the numerical methods, we usually convert (4) or (5) to a set of coupled radial equations by making a single-center(SC) expansion of the bound and continuum functions of the form

$$F_\alpha(\vec{r}) = \Sigma f_\Gamma(r) Y_{l_\alpha m_\alpha}(\Theta,\phi) , \qquad (12)$$

where Y is a spherical harmonic, and by then integrating over all angular coordiantes. The scattering channel is labeled by $\Gamma = (\alpha, l_\alpha, m_\alpha)$ with α representing the quantum numbers of the target, l_α, the orbital angular momentum of the continuum electron, and m_α, its projection on the internuclear axis. Much aspersion has been heaped upon SC methods for bound-state problems and with justification since the form of the electronic wavefunction near the nuclei is critical to detemining the energy. However, for scattering, the nuclear singularity is less important, and with proper care SC expansions can yield highly reliable results.

At this juncture, we can work with either the differential or integral equations. The differential equations are usually solved by propagation schemes based on finite difference approximations. The exchange terms,as always, present an additional complication due to their nonlocal nature. We overcome this problem either non-iteratively by introducing additional DE's for the nonlocal terms or iteratively by starting with an approximation for f and the making successive substitutions until convergence is reached. The integral equations may also be solved by direct propagation schemes with the nonlocal terms treated in a similar fashion. Variational prescriptions based on the Kohn procedure and using numerical trial functions have also been developed.

Finally, we should note that methods have been devised for diatomic systems by which a quadrature is introduced for both the radial and angular variables. This prescription leads to a set of coupled partial DE's, which can in turn be converted to banded matrix equations. Correlation effects have been introduced through polarized orbitals.

We better illustrate the numerical forms of solution by considering the linear algebraic(LA) method. We work in the IE formulation and make a SC expansion to obtain a set of coupled radial integral equations,which are labeled by the channel index Γ. We employ strategy S2 by imposing log-derivative boundary conditions at a particular radial point,a,which is selected to enclose the region of stong,nonlocal interactions. Inside $r=a$, we invoke the full LA formation and match to solutions at the boundary determined by simple propagation in the outer zone. In the inner region, we also follow strategy S3 and solve for the P-space solution through an effective optical potential. We now convert to a set of matrix equations by introducing a discrete quadrature of η radial points for the integrals and functions. The resulting set of LA equations is of the form:

$$\underline{M}\,\underline{f} = \underline{g} \quad , \tag{13}$$

where the matrix M is of order $O = \eta \times m$, the vectors f and g are of length O, and m is the number of channels in P-space. Each element of the solution vector f is designated by a channel Γ and a discrete radial point. Such linear systems can be efficiently solved by iteration-variation techniques(Schneider and Collins,1986a), which do not require the storage of the full matrix. This approach has two clear advantages: 1) the order of the matrix is not increased by the nonlocal terms and 2) the solution is determined at all points simulataneously. In addition, this procedure takes full advantage of the new vector and multi-tasking computers. We generally construct the optical potential from an entirely square-integrable basis. This approximation to the continuum function allows us to determine this term directly from standard CI molecular-structure programs, especially when we combine the procedure with a separable representation(S4). In addition, the method has been used in conjunction with variationally derived polarization- correlation potentials(Gibson and Morrison,1984).

L^2 Methods

In the L^2 approach, we obtained a solution to (4) by expanding in terms of a set of known functions as

$$\psi(\vec{r}) = \sum_i c_i \, \phi_i(\vec{r}) \quad . \tag{14}$$

Many different forms of these functions have been explored. In analogy with bound-state problems, Slater- and Gaussian-type orbitals(STO and GTO) were first used. This approach has the distinct advantage of utilizing the full panoply of molecular structure programs, which have a long history of development. On the other hand, such basis functions, which efficiently represent the multi-center nature of the wavefunction near the nuclei, have difficulty in tracing the oscillatory form of the scattering solution in more extended regions. For this reason, most square-integrable methods now employ in addition to a GTO basis one that better represents this oscillatory behavior. Such augmented bases are constructed from either numerical functions, which satisfy some model potential, or analytical functions, such as bessel, to better represent the continuum solution. For a simple potential, we have a detailed comparison of thirty-five square-integrable methods(Staszewska and Truhlar,1987). Unfortunately for more complicated interactions, such tests are not available.

Although methods, such as the T-matrix, can arise from a direct expansion of the potential in the LS equations in terms of the finite basis, we derive most of the L^2 methods discussed below from variational prescriptions. For the variational methods, we consider a functional $I[\psi_t]$ of a trial function ψ_t. One particular example is

$$I[\psi_t] = \langle\psi_t| (H - E)| \psi_t\rangle \quad , \tag{15}$$

where the trial function satisfies a prescribed asymptotic boundary condition. The functional has the properties that 1) for the exact solution $I[\psi] = 0$ and 2) for small variations($\delta\psi$) in the trial function, $\delta I = 0$ (stationary). Many variational pronciples have been devised ; however, we shall confine our attention to two major approaches in which the functional is defined: 1) over a limited spatial volume or 2) over all space.

The R-matrix, eigenchannel, and finite-volume methods, which form the principal approaches of the first class, differ in details but basically follow a common philosophy. We illustrate these techniques by concentrating on the R-matrix(RM) prescription. The R-matrix simply relates the wavefunction to its derivative

$$\psi(r) = - R \frac{d}{dr}[\psi(r)] \tag{16}$$

We begin with strategy S2 and apply arbitrary boundary conditions at a finite surface,Σ. Within this surface, we represent the solution by (7) and thus follow strategy S3. The boundary condition effectively converts the scattering problem in the inner region into a bound-state one of the form of (10). We then expand in terms of a set of discrete functions(14),which satisfy the eigenvalue equations

$$H_b |\phi_i) = \epsilon_i |\phi_i) \quad . \tag{17}$$

We write a formal soultion to (6b) as

$$|\psi) = (H_b - E)^{-1} L_b |\psi) \quad . \tag{18a}$$

and by inserting a complete set of eigenfuctions defined by (17), we have

$$|\psi) = -\sum_i \frac{|\phi_i)(\phi_i | L_b | \psi)}{(E - \epsilon_i)} \tag{18b}$$

Evaluating this at the surface, using the properties of the Bloch operator, and noting the defintion of the R-matrix, we find

$$R = \sum_i \frac{\phi_i(\Sigma)\,\phi_i^*(\Sigma)}{(E - \epsilon_i)} \quad , \tag{18c}$$

where $\phi(\Sigma)$ schematically represents evaulation of the function at the surface. Since the eigenfunction solutions (17) are independent of the scattering energy, E, we need only solve the eigenvalue equations once in the inner region. The R-matrix can then be determined over a extensive set of energies from (18c) very economically . By matching to known solutions from the outer region, we derive the scattering information.

Many variational prescriptions have been evolved for treating the scattering problem over all space. Some are based on the solutions to the DE's such as the Kohn and Hulthen methods while others like the Schwinger arise from the IE's. Several forms of the Kohn, based on real-value trial functions(K-matrix boundary conditions) are in use although they all suffer from spurious singularities. This problem appears to be rectified by using out-going(complex)solutions and moving these poles off of the real axis. In addition, complex variational prescriptions have been developed in which the standard trial function expansion is augmented by complex basis functions(CBF). These functions, which have components of the form exp($i\alpha r$), contain the flexibilty to represent the oscillating continuum part. This choice of basis functions allows scattering quantities to be calculated from standard bound-state programs with some modifications. In addition, projection-operator formalisms have been successfully applied, especially for resonances.

At present the Schwinger(SV) approach has received the most attention. We seek an approximate solution to the LS equations in terms of a set of discrete basis functions($|\alpha\rangle$). To this end, we employ a special form of a separable potential(S4)-

$$V(\vec{r}|\vec{r}') = \sum_{\alpha,\beta} \langle\vec{r}|V|\alpha\rangle\, [V^{-1}]_{\alpha\beta}\, \langle\beta|V|\vec{r}'\rangle, \qquad (19)$$

where the V^{-1} term signifies the inverse the matrix element $\langle\alpha|V|\beta\rangle$. We then substitute this potential into the LS equation (5e) and obtain the following expression for the T-matrix:

$$\langle\vec{k}|\ T\ |\vec{k}'\rangle = \sum_{\alpha,\beta} \langle\vec{k}\ |\ V\ |\ \alpha\rangle\ [D^{-1}]_{\alpha\beta}\ \langle\beta\ |\ V\ |\ \vec{k}'\rangle \quad , \qquad (20a)$$

where

$$D_{\alpha\beta} = \langle\alpha\ |\ V - V\,G_o^{+}\,V\ |\ \beta\rangle\ , \qquad (20b)$$

and k(k') is the initial(final) wavenumber of the continuum electron. This form of the transition matrix is equivalent to the Schwinger variational expression for a trial wavefunction expanded in the same basis. Therefore, this form of the T-matrix possesses all of the stability properties of the usual SV method. Since the trial function is always found in combination with the potential the basis need only have the range of V. Therefore, unlike the Kohn-type methods, the Schwinger functions are not required to satisfy the asymptotic boundary conditions. The method can be refined through an iterative presciption by which the numerical solutions are used as a new trial wavefunction. The method has been extended to multi-channel problems by working in terms of a projected LS equation(S3) and modified variational principles. Other related prescriptions, such as the C-functional, have also been developed.

The above section serves only to give a flavor of this robust and exciting field with a variety of very different approaches available to tackle the many difficult problems encountered.

"This particularly rapid, unintelligable patter
isn't generally heard, and if it is, it doesn't matter" - Ruddigore

COMPARISON OF METHODS

In this section, we give a brief comparison of the various methods discussed in the previous section. We shall concentrate on those systems that have been treated by several methods so that we may draw some conclusions on the efficacy of the various approaches.

Hydrogen Molecular Ion H_2^+

This forms the simplest molecular target from which we can scatter electrons. Since we only have a two-electron system, we expect that all of the methods can be carried to a high level of convergence. We consider an electron incident on the ion with an energy below the first excitation threshold($1\sigma_u$). Only elastic scattering is possible; however, we do encounter Feshbach resonances arising from the temporary trapping in the doubly-excited states of the compound system H_2. For scattering in the $^1\Pi_u$ symmetry, the lowest such resonance series is of the form $1\sigma_u n\pi_g$ and converges on the $1\sigma_u$ state of the ion. Other such series, associated with higher excited states, may interfere with this one giving rise to spectacular changes in the resonance width, which is related to the trapping time. In Table 1, we compare the resonance widths as a function of internuclear separation,R, in the linear algebraic (LA), R-matrix(RM), and complex basis function(CBF) approaches(Collins et al.,1986). We employ two forms of the LA method: 1) a n-state CC in which correlation functions are used only to relax the strong orthogonality constraint (LACC) and 2) a single P-space state augmented by an effective optical potential(LAOP). We note that the agreement is excellent for this sensitive quantity. We find comparable agreement among the methods for the positions. The situation is somewhat different for the $^1\Sigma_g$ symmetry. We still have very good agreement on the widths and positions; however, the LACC approach has a much slower convergence. This reinforces our initial dictum to maintain the greatest flexibilty in the P and Q spaces. These resonances can have profound effects on the photoionization cross sections(Raseev,1984;Noble and Burke,1986b).

Table 1. Comparison of Resonance Widths Γ(meV) for the lowest $^1\Pi_u$ Resonance

Below the First Excited State for $e^- + H_2^+$ Collisions

method		R(a_0)	
	0.80	1.20	2.00

LACC			
n=4	100.45	14.03	11.88
6	85.56	13.65	12.06
8		15.31	12.34
LAOP	100.8	14.35	11.35
RM	90.52	12.96	11.02
CBF		10.96	13.67

Target nCC bases: 4CC,[$1\sigma_g$,$1\sigma_u$.$1\pi_u^{\pm}$]; 6CC,[4CC,$2\sigma_{g,u}$]; 8CC,[5CC,$2\sigma_u$.$1\pi_g^{\pm}$]
References: (Collins et al.,1986; Schneider et al.,1987)

Hydrogen

The next simplest system to consider is molecular hydrogen. In Fig. 1., we have already shown that the LA method is capable of reproducing the most salient features of the low-energy elastic scattering. The agreement with other ab initio methods, such as the Schwinger and R-matrix, is excellent(see Gibson et al,1984). In addition, model potential representations of the polarization-correlation effects give reasonably good results(Gibson and Morrison,1984). Calculations have also been performed for inelastic scattering. The most strigent test for the methods arises for singlet-triplet transitions, since the coupling terms dependent only on the exchange interaction. In Fig. 2, we present the total inelastic scattering cross section as a function of electron energy for the excitation from the ground to the first excited triplet state. We compare the SV(Lima et al.,1985), RM(Baluja et al.,1985), and LA(Schneider and Collins,1985) methods and find excellent agreement. The LA and SV calculations were performed at a two- state level while the RM results included some extra correlation functions. The lower curve represents an LA calculation in which the strong orthogonality constraint is invoked but no terms are introduced into Q-space to relax this condition. This case corresponds to several older calculations(Chung and Lin,1978;Weatherford,1980) and demonstrates the need to include all allowed relaxation effects in such calculations. The agreement with experiment (Nishimura and Danjo,1986;Khakoo et al.,1987) is also quite good.

Nitrogen

The situation in nitrogen is not as clear. For the $^2\Pi_g$ symmetry, which has a well-known shape resonance at about 2 eV, several methods have successfully reproduced the vibrational structure observed in the elastic scattering cross section. Results with the R-matrix method(Schneider et al.,1979;Morgan,1986) in which nonadiabatic terms were introduced directly into the formal equations yielded quite good agreement with experinment and with other prescriptions (Berman et al.,1983). A recent Schwinger multi-channel calculation(Huo et al.,1987a) using the projection-operator techniques also produced the structure in the vicinity of the resonance. Therefore, for the resonance symmetry, the ab initio methods are in reasonably good agreement and are capable of being extended beyond the AN level to produce vibrational structure.

For the $^2\Sigma_g$ scattering symmetry the situation is less propitious. For energies above a few eV, we have fairly good agreement among the various methods. However, at lower energies, we encounter significant differenences between the RM(Burke et al.,1983) and the LA(Schneider and Collins,1984) and SV(Huo et al.,1987b) methods. This disagreement can most readily be observed in Fig. 3. We also plot the experimental results of Kennerly(1980) for the total integrated cross section. The comparison at very low energies is valid since the dominant component is the sigma gerade. The source of the differences is not precisely certain. The SV and LA results are within about fifteen percent for the range of energies presented. However, they exhibit different shapes at the very low energies. This behavior may arise from the treatment of the long-range polarization terms. These terms are explicitly included in the LA calculations but are difficult to obtain in the SV since basis functions must span a reasonably large space. The results are very sensitive to the types of correlation used in (8) and to the form of the expansion basis(Schneider and Collins,1984). None of the methods includes correlation of the target function explicitly. The case may be similar to one encounter in atomic scattering in which a delicate balance between bound and continuum correlation had to be struck in order to produce accurate cross sections. This situation will only be rectified by more elaborate calculations, which can systematically vary the amount of correaltion in each part and the size of the basis. We should also point out that two model potentials(Padial and Norcross,1984;Morrison et al.,1987) are in better agreement with the experiment than any of the "*ab initio*" methods.

While disagreements still exit in some cases amongst the methods, the situation is encouraging for treating the direct,exchange,and correlation effects in a consistent fashion for moderately-sized molecular systems.

STATE OF THE FIELD

In this section, we attempt to present the current capabilities in accurately solving the Schrodinger eqution for electron-molecule collisions. This presentation is to some extent subjective and will certainly be out-of-date by publication time. This is an unfortunate situation for the authors but a very good one for the field since it demonstates a vitality and sense of profound progress. Many of these methods are in an inchoate phase, and the next few years should witness a vast extention of our ability to accurately handle electron collisions. We make a somewhat artificial division based the the form of the interaction.

Static and Local Potentials

At present, for electronically elastic scattering, we are able to treat static and static+local model potentials for polyatomic systems having up to third-row atoms. In many cases, these local potentials effectively model both exchange and correlation effects(Morrison and Collins,1981;Onda and Truhlar,1980) and have been extended to treat rovibrational excitations. Some local formulations for electronic excitation have been devised, but their development lags considerably behind the elastic methods.

Static-exchange

In the SE approximation, we take only a single state in expansion(3) and treat only the direct and exchange terms. The correlation effects must come from the interaction with other states and are therefore omitted. This is a fairly restrictive definition since some autheors use SE interchangably with CC. Exact SE calculations have been performed for a wide variety of first- and second-row diatomic and polyatomic molecules. Such systems as H_2, N_2, CO, NO, CN, Li_2, LiH, LiF, HCl, HF, F_2, HCN, H_2O, and CH_4 have received routine treatment. While correlation effects play an important role for neutrals, the SE approximation seems much better for electron-ion collisions in which the long-range Coulomb term plays an important role. Thus, the approximation gives substantially better results for photoionization.

Static-exchange + polarization

For elastic collisions, optical potentials and closed-channel CC schemes have been devised to account for the correlation effects. Thses methods have been particularly effective at low energies in which all but one channel is closed. Such calculations have been applied to H_2^+, H_2, NO, NO^+, and N_2.

Electronic excitation

Only in the past few years have the *ab initio* techniques been honed to effectively treat electronic excitations although some pioneering work extends back over a decade. The approaches have been applied to several systems including H_2^+, H_2, N_2^+, and O_2. Except for the smallest systems, the calculations have been limited to a very few states. For hydrogen, upto ten-state CC calculations have been performed.

Remaining Problems

Certain problems cited above such as the disgreement among methods for a particular system can probably be resolved within the present form of these procedures, requiring careful and systematic convergence tests. However, one situation remains, which continues to plague atomic collisions also, namely the introduction of pseudoresonances through limitations on the basis expansions. If we could include all target states in (3) necessary for convergence, then we would never encounter these specious resonances. For low-energy collisions, a few isolated states may be sufficient to describe the scatteing event. However, as the energy of the electron increases, more and more states become accessable. For energies of a ten eV or more, hundreds of channels may be open. Clearly, even with the great advances in formulations and computer technology, such large expansions are not feasable. The standard remedy is to represent the effects of the higher channels by a few well-chosen pseudostates. While reducing the size of the calculation to a tractable form, these states give rise to spurious resonances. Several prescriptions have been developed to remove the effects of these resonances by analytically continuing into the complex plane and performing certain restricted averaging(Burke et al.,1981;Slim and Stelbovics,1987). However, at present, we do not have a Formally systematic means for practically overcoming this problem.

" If this is not exactly right, we hope you won't upbraid.
You can't get high esthetic tastes, like trousers, ready made.
Insight into 'scattering', time alone will bring,
But as far as we can judge, it's something like this sort of thing."
Patience(with liberty)

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APPENDIX

In this appendix, we list the major *ab initio* methods for treating electron- molecule collisions. The selection is by no means exhaustive but is representative of the field. In citing sources for each technique, we have tried to follow a pattern. We have attempted to include an early paper that outlines the general procedure and a later one that gives a recent application. If we authors have been diligent in referencing their earlier works(which they usually are), the latter citation should allow a trace of the intervening material. We place special emphasis, of course, on those methods in cuurent use. We generally include calculations at the static-exchange level or higher.

Method	Authors
Schwinger Variational(SV)	Watson,Lucchese,McKoy,Rescigno(1980)
	Lynch,Lee,Lucchese(1984)
	Lucchese,Takatsuka,McKoy(1986)
	Gibson,Lima,McKoy,Huo(1987)
	Berman/Kaldor(1981)
	Berman,Walter,Cederbaum(1983)
R-matrix(RM)	Schneider(1975)
	Schneider,LeDourneuf,VoKyLan(1979)
	Burke,Mackey,Shimamura(1977)
	Noble/Burke(1986a)
	Schneider,LeDourneuf,Burke(1979)
	Nesbet,Noble,Morgan(1986)
	Holley,Chung,Lin(1982)
Linear Algebraic(LA)	Collins/Schneider(1981,1984)
	Schneider/Collins(1986a,b)
	Padial and Norcross(1984)
	Morrison,Gibson,Saha(1987)
Complex Basis Function(CBF)	McCurdy,Rescigno,,Davidson, Lauderdale(1980)
	Yabushita/McCurdy(1986)
C-functional	Lee,Takatsuka,McKoy(1981)
	Basden/Lucchese(1986)
T-matrix	Rescigno,McCurdy,McKoy(1974)
	Fliflet,Levin,Ma,McKoy(1978)
	Klonover/Kaldor(1973)

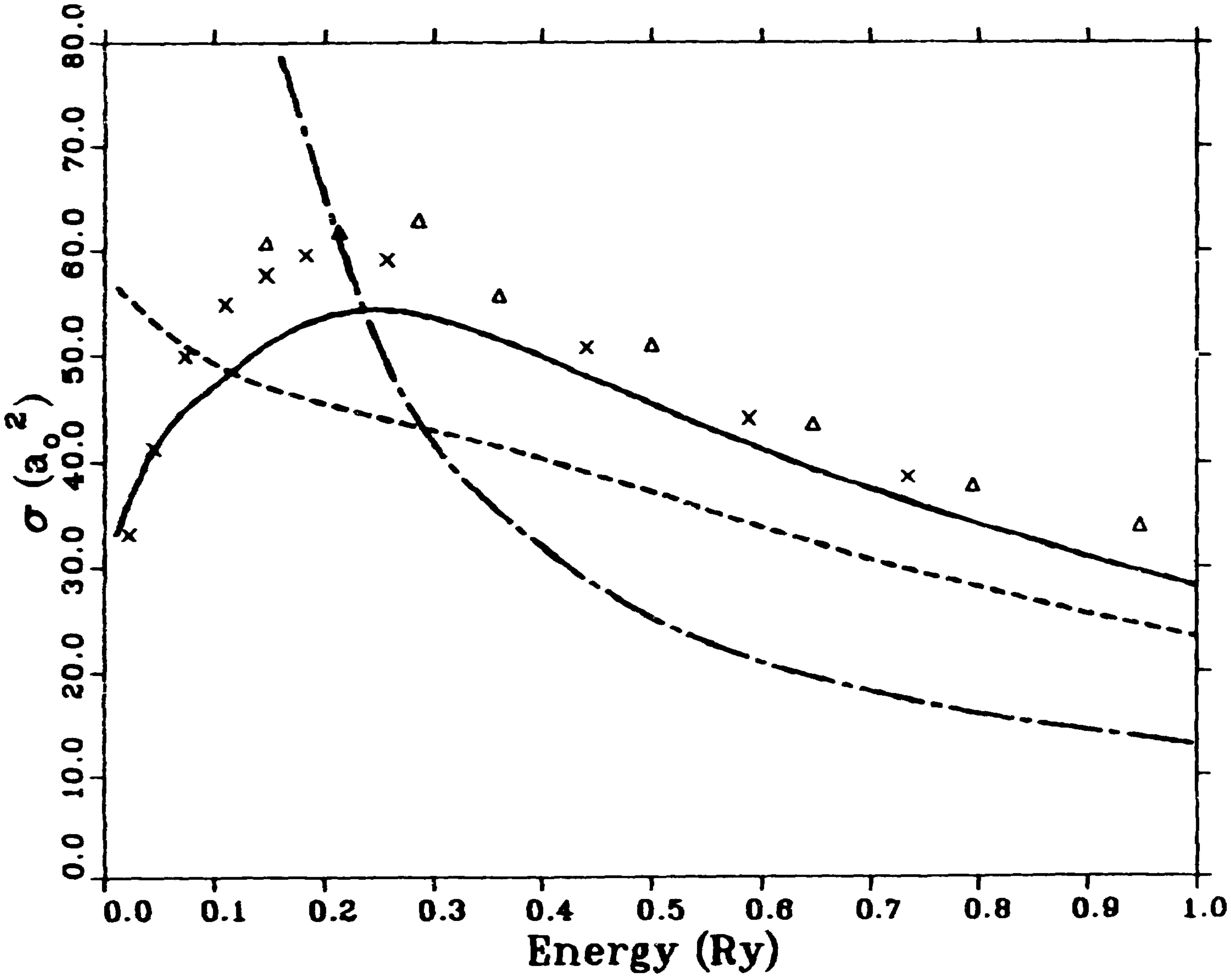
Finite Volume(FV)	LeRouzo/Raseev(1984) Raseev(1985)
Kohn variational	
Real	Takagi/Nakamura(1973) Collins/Robb(1980)
Complex	Rescigno,McCurdy,Schneider(1987)
Integral equations(IE)	
Iterative	Collins,Robb,Morrison(1980)
Non-iterative	Rescigno/Orel(1981)
Differential equations(DE)	Henry/Lane(1969) Chung/Lin(1978) Raseev(1980)
Partial DE's(PDE)	Onda/Temkin(1983) Weatherford,Onda,Temkin(1985)
Projection operator	Hazi(1978) Berman,Estrada,Cederbaum, Domke(1983) Hara/Sato(1984)
Polarized Orbital	Temkin/Vasavada(1967) Chandra(1986)

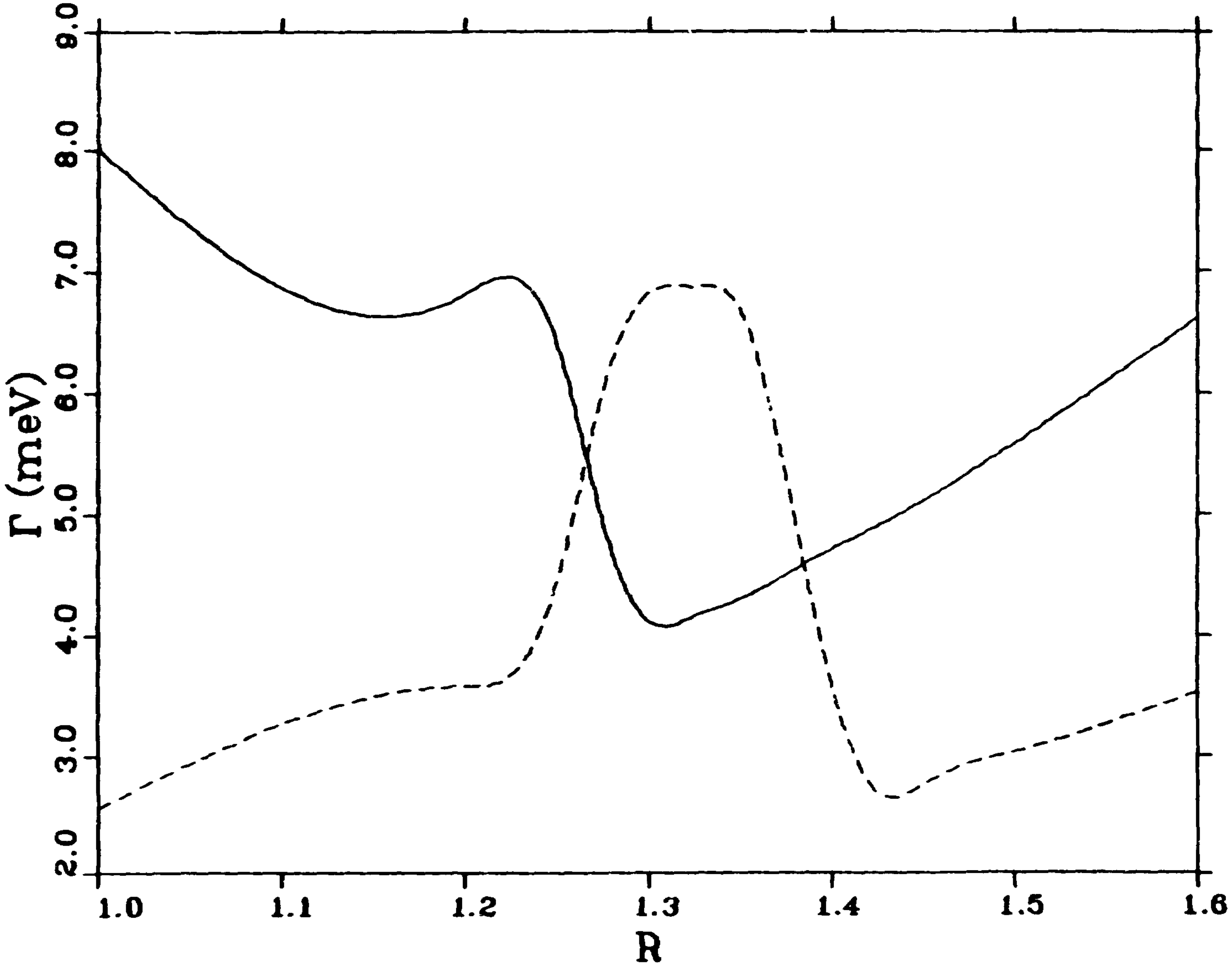
Fig.1. Comaprison of theoretical and experimental total elastic $e^- + H_2$ cross sections as a function of electron energy. Theoretical results: chain - staic(S); dash - static-exchange(SE); line - SE+polarization(SEP). Experimental results: triangles - Hoffman et al.(1982); cross - Dalba et al.(1980)

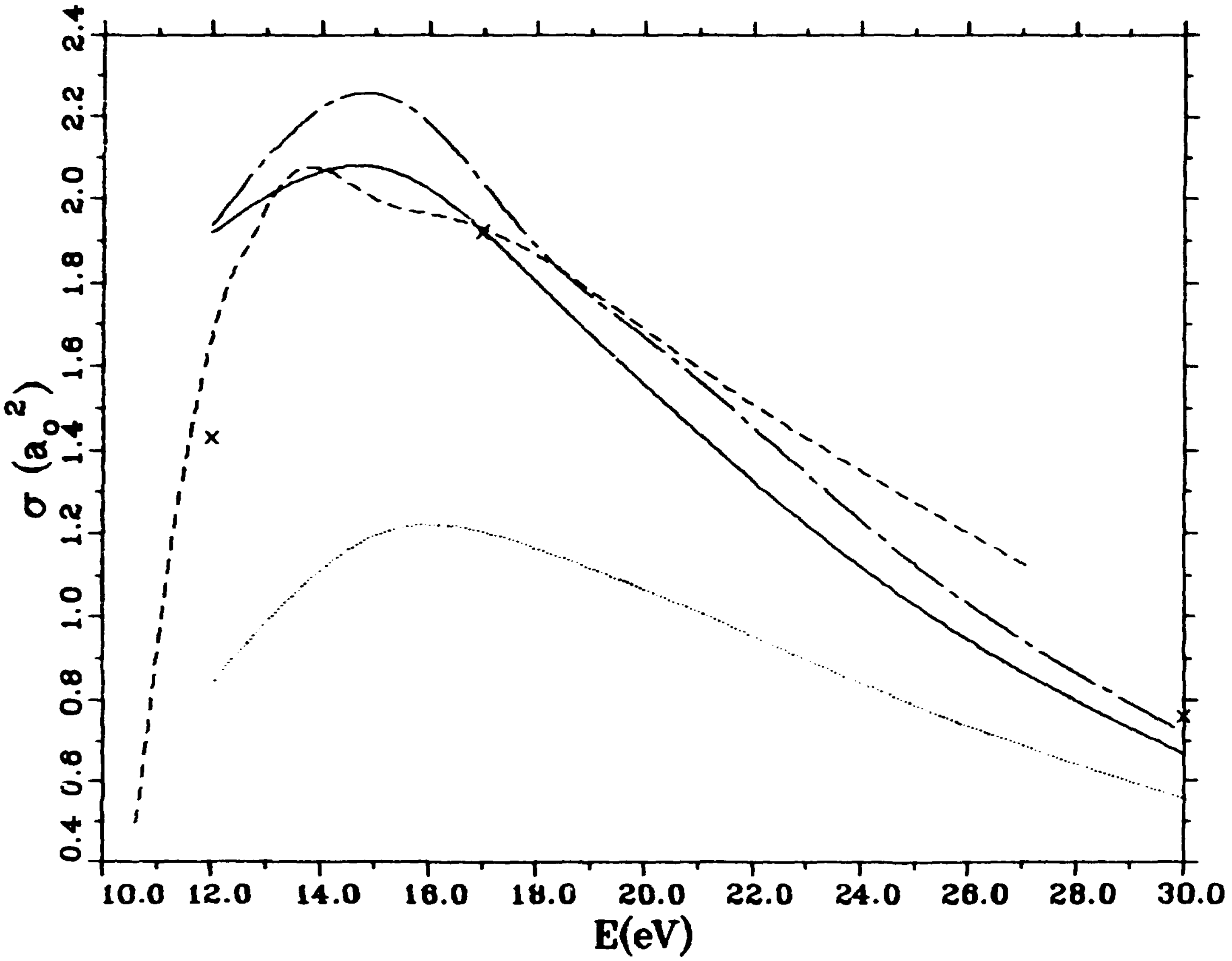
Fig. 2. Resonant widths as a function of internuclear distance,R, for $e^- + H_2^+$ scattering below the first excitation threshold($1\sigma_u$) for $^3\Pi_u$ symmetry. Nomenclature: line - lowest resonance; dash - second resonance.

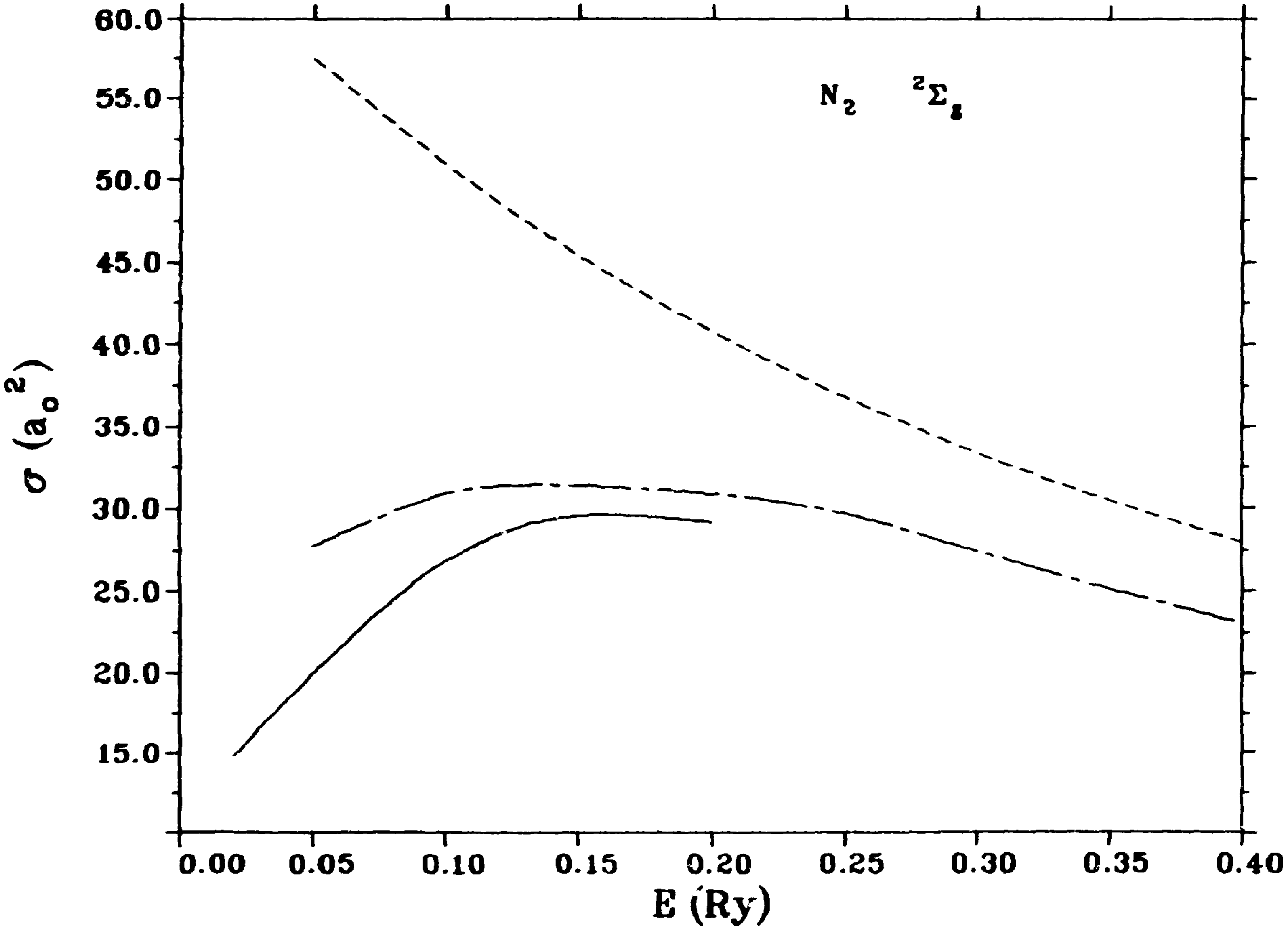
Fig.3. Comparison of theoretical methods and experimental results for electron impact excitation of molecular hydrogen Theoretical results: line - LA(Schneider and Collins,1985); dash - RM(Baluja et al.,1985); chain - SV(Lima et al.,1985); cross - LA,no correlation. Experimental: cross - Nishimura and Danjo(1986).

Fig. 4. Comparison of theoretically determined integrated cross sections(a_0^2) for electron scattering fron molecular nitrogen in the $^2\Sigma_g$ symmetry. Nomenclature: line - LA(Schneider and Collins,1984); dash - RM(Burke et al.,1983); chain - SV(Huo et al.,1987). Experiment: cross - Kennerly(1980), total cross section.


0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
σ (a_o^2)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Energy (Ry)


Γ (meV)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1.1
1.2
1.3
1.4
1.5
1.6
R


$\sigma\ (a_o^2)$
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.8
0.4
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
28.0
30.0
E(eV)


N_2 $^2\Sigma_g$
σ (a_o^2)
60.0
55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
E (Ry)