

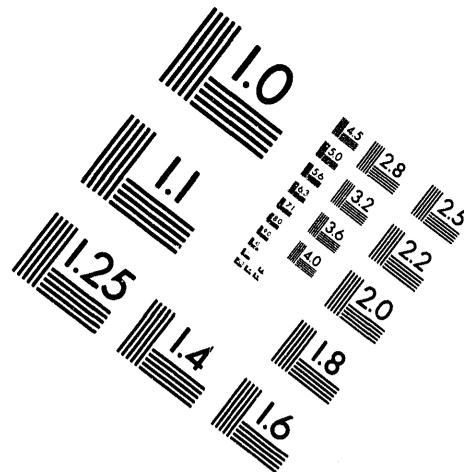
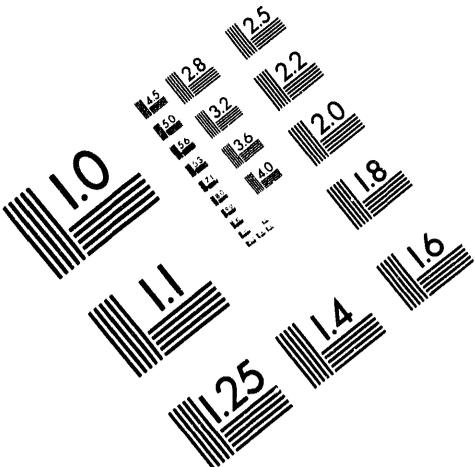


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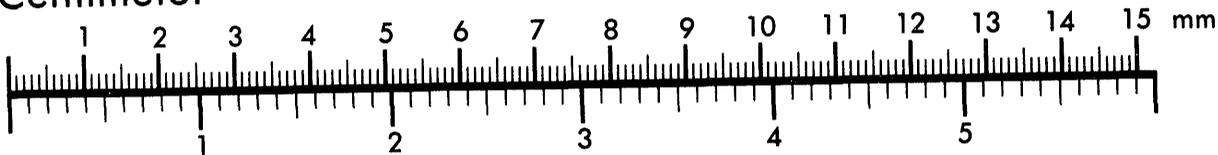
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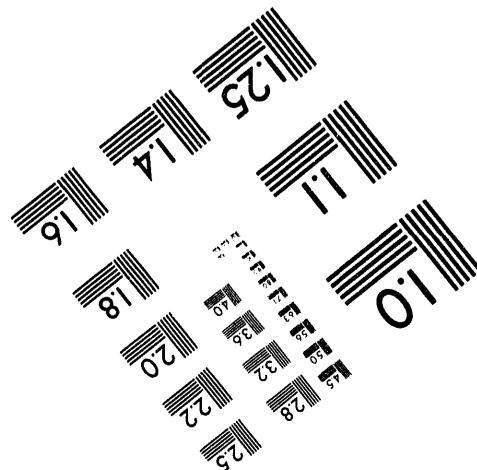
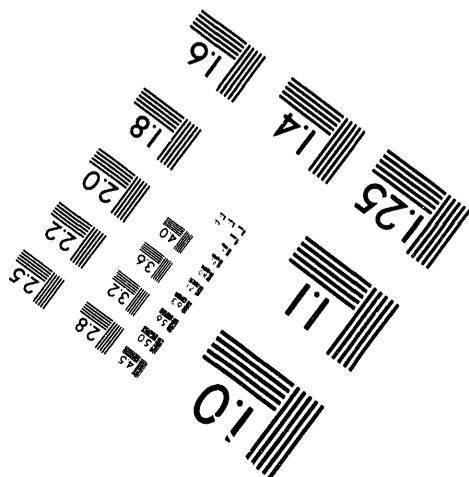
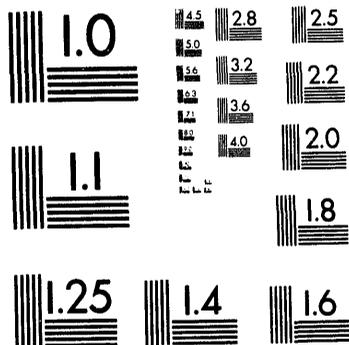
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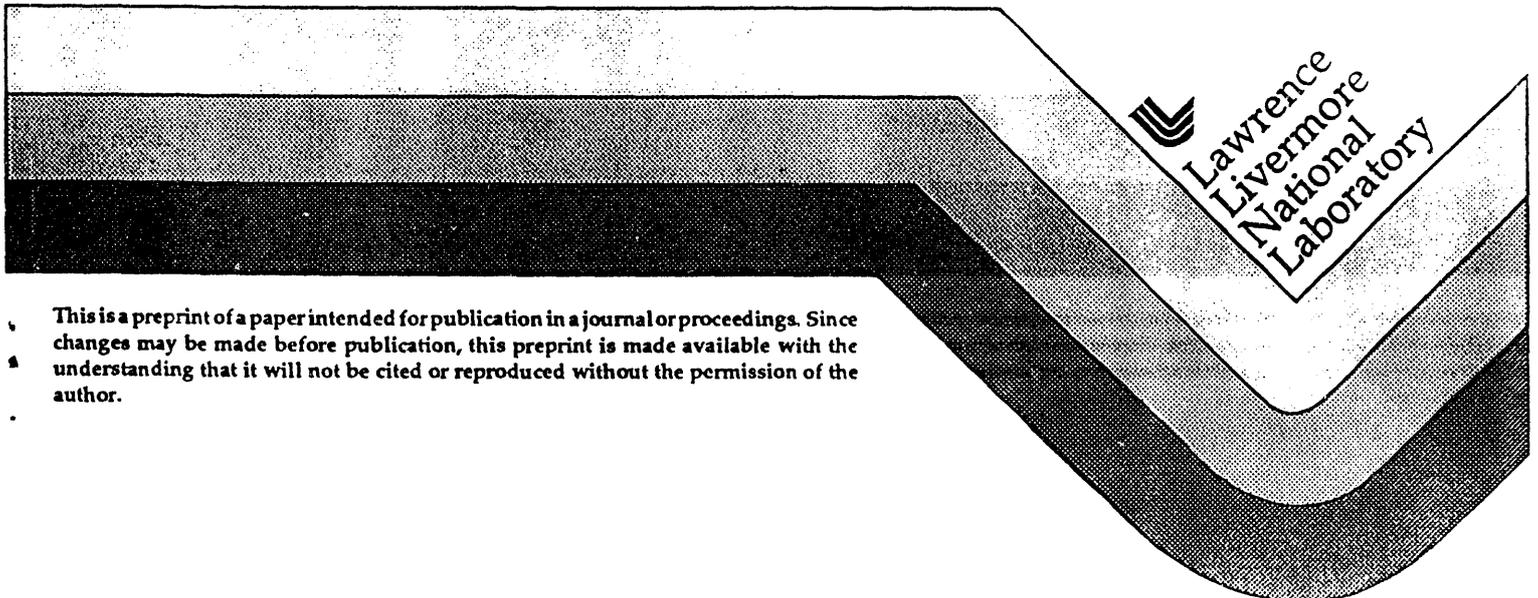
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**RELATIVISTIC CONFIGURATION-INTERACTION
CALCULATION OF THE CORRELATION ENERGIES OF
HELIUMLIKE IONS**

**KWOK-TSANG CHENG and MAU HSIUNG CHEN and
WALTER R. JOHNSON**

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RELATIVISTIC CONFIGURATION-INTERACTION
CALCULATION OF THE CORRELATION ENERGIES
OF HELIUMLIKE IONS *

KWOK-TSANG CHENG and MAU HSIUNG CHEN

*University of California, Lawrence Livermore National Laboratory
Livermore, California 94550, USA*

WALTER R. JOHNSON

Physics Department, University of Notre Dame, Notre Dame, Indiana 46556, USA

ABSTRACT

A new relativistic configuration-interaction (CI) method using B-spline basis functions has been developed to study the correlation energies of two-electron heliumlike ions. Based on the relativistic no-pair Hamiltonian, the CI equation leads to a symmetric eigenvalue problem involving large, dense matrices. Davidson's method is used to obtain the lowest few eigenenergies and eigenfunctions. Results on transition energies and finite structure splittings for heliumlike ions are in very good agreement with experiment throughout the periodic table.

1. Introduction

In this work, we present a new relativistic configuration-interaction (CI) method for atomic structure calculations using finite basis sets constructed from B-spline functions of piecewise polynomials. This method is used to calculate the correlation energies of the low-lying $n = 1 - 2$ states of two-electron heliumlike ions with nuclear charges ranging from 4 to 100. These calculations were undertaken both to provide accurate term energies for heliumlike ions and to develop the computational techniques necessary to carry out large-scale, relativistic correlation calculations for atoms and ions with complex atomic structure.

The CI method, also known as the exact diagonalization method, is a large-scale, variational calculation widely used in atomic, molecular, nuclear, and solid state physics to study correlation effects. Relativistic CI calculations, however, are not as widely used, as they are more difficult to carry out than the corresponding nonrelativistic ones. One reason is the big increase in the number of configurations, and hence the computational effort, from nonrelativistic to relativistic CI

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calculations. A more fundamental problem involves the existence of the negative-energy states in the relativistic spectrum which leads to the *continuum dissolution* problem in perturbation theory when one of the electrons in a many-electron system is excited into the positive-energy continuum while another electron falls into the negative-energy continuum with the same excitation energy.^{1,2} Even for single-electron systems, spurious states can appear in relativistic basis set calculations, resulting in the *variational collapse* of the ground and excited states.³ To date, most of the relativistic CI calculations of atomic structures are carried out with positive-energy Dirac-Fock or Dirac-Slater basis functions. While they don't suffer from the above mentioned problems, accuracy of their results is nevertheless limited because of the neglect of the positive-energy continuum in these calculations. All these difficulties in relativistic CI calculations are largely avoided in our present approach and excellent results were obtained on the term energies of the low-lying states of heliumlike ions.

2. Theory and Calculation

Our calculation is based on the relativistic no-pair Hamiltonian from quantum electrodynamics (QED):^{2,4}

$$H = H_0 + \Lambda_{++}(H_C + H_B)\Lambda_{++}, \quad (1)$$

where H_0 is the sum of single-particle Dirac Hamiltonians, H_C and H_B are the Coulomb and retarded Breit interactions, respectively, and Λ_{++} is the positive-energy projection operator introduced to guard against the continuum dissolution problem. Eigenfunctions of the Hamiltonian are expanded in a basis of two-electron configuration-state-functions (CSF) constructed from anti-symmetrized products of one-electron orbitals. Eigenenergies and eigenfunctions of the low-lying two-electron states are then determined by diagonalizing the Hamiltonian matrix.

The one-electron basis orbitals used here are B-spline solutions of the Dirac equation for an electron in a Coulomb field constrained to a finite cavity.⁵ Spurious states in the spectrum are avoided by imposing proper boundary condition based on the MIT bag model. The B-spline basis set is finite and complete. The resulting modified Dirac spectrum consists of a finite set of discrete eigenstates which separate cleanly into equal numbers of positive- and negative-energy states. The positive-energy branch contains terms that belong to the bound-state spectrum as well as the positive-energy continuum of the unmodified Dirac spectrum. As a result, the use of this B-spline basis set in a CI calculation effectively includes interactions with the bound states as well as with the positive-energy continuum for highly accurate results. Furthermore, by including only the positive-energy solutions of the modified Dirac equation in our CI calculations, positive-energy projection operators in the relativistic no-pair Hamiltonian are implicitly included.

The CI equation leads to a large, symmetric eigenvalue problem. In this work, the number of configurations used ranges from a few hundred to well over eight thousand. The Hamiltonian matrix is dense, in contrast with the molecular or nuclear cases, where the matrix is often much larger but sparse. Eigenvalues and eigenvectors for the lowest few states are determined using Davidson's method.^{6,7} This is an iterative method based on perturbation theory and is very efficient for diagonally dominated CI matrices with very fast rate of convergence. Also, only two

vectors have to be kept in the computer core for the method to work, making the diagonalization of big CI matrices possible on machines with relatively small core memory. On the CRAY-YMP supercomputer at the Livermore Computer Center, our CI matrices can reside on the core and the diagonalization of these matrices with Davidson's method is very fast and takes no more than a few minutes of cpu time. The evaluation of the Hamiltonian matrix, on the other hand, is much more time consuming. Efficient algorithms have been developed to speed up the calculation of angular recoupling coefficients and Coulomb and Breit integrals by at least an order of magnitude. Even so, forty to fifty hours of CRAY-YMP time are required for each heliumlike ion considered.

In this study, a cavity size of 8 a.u. was used for Ne^{8+} and a $1/Z$ scaling rule was used to determine the cavity radius for other ions. In general, results are not sensitive to the choice of cavity radii. While 40 positive-energy B-spline orbitals were generated for each of the s, p, d, \dots states inside the cavity, only the first 20 to 25 orbitals were used in the CI calculation to reduce the computational effort. The use of these truncated B-spline basis sets was found to have negligible effect on the accuracy of our results. For the $n = 2$ triplet states, our B-spline basis sets typically include all orbitals with $\ell = 0 - 5$ (s, p, d, f, g, h). For the $n = 1$ ground state and the $n = 2$ singlet states, convergence of the CI energy as a function of ℓ is much slower and the B-spline basis sets were extended to include orbitals up to $\ell = 8$. Residual corrections from higher- ℓ states were obtained by extrapolations. Further details of the theory and computational method are given in Ref. 8.

3. Results and Discussions

We have calculated the term energies for the $n = 2$ triplet states of helium-like ions with our relativistic CI method. Mass polarization and QED corrections are obtained from Drake's unified method.⁹ Our term energies are in very good agreement with the relativistic many-body perturbation theory (MBPT) results of Johnson and Sapirstein.¹⁰ Discrepancy with Drake's results is due largely to the neglect of higher-order relativistic corrections in Drake's calculation. Our results on transition energies and fine structure splittings agree very well with experiment throughout the periodic table. Examples are shown in Table 1. Detailed results and discussions can be found in Ref. 8.

Table 1: Comparison between theory and experiment on transition energies.

Z	This work	Drake ^a	MBPT ^b	Experiment	Ref.
$1s2p\ ^3P_0 - 1s2s\ ^3S_1$ in cm^{-1}					
5	35393.608(30)	35393.736(70)		35393.627(13)	11
36	356828	357330	356823	357400(260)	12
92	2038700	2069900		2097000(64000)	13
$1s2p\ ^3P_0 - 1s2p\ ^3P_1$ in eV					
47	0.788	0.933		0.79(4)	14
64	18.548	19.082		18.57(19)	15

^aDrake, Ref. 9

^bJohnson and Sapirstein, Ref. 10

We have also calculated the term energies for the $n = 1, 2$ singlet states of heliumlike ions. In this case, QED corrections, including screening and relaxation effects, are calculated with a scheme by Cheng *et al.*¹⁶ instead of taken from Drake's calculation. Our correlation energies are in very good agreement with the relativistic all-order equation results of Plante *et al.*¹⁷ For the K_{α} x-ray energies, discrepancy between our results and Drake's results comes partly from differences in correlation energies and partly from differences in QED corrections. Our transition energy results also differ slightly from those of Plante *et al.* who use Drake's QED corrections in their all-order calculations. Including orbital relaxation effects in our QED corrections seems to improve the agreement between theory and experiment. However, residual differences exist and are likely due to higher-order QED corrections not yet considered in any theoretical calculations. Examples of the comparison between theory and experiment on the K_{α_1} x-ray energies are shown in Table 2. Detailed results and discussions are given in Ref. 18.

Table 2: Theoretical and experimental K_{α_1} x-ray energies (eV).

Z	This work	Drake ^a	All order ^b	Experiment	Reference
18	3139.62	3139.58	3139.58	3139.55(4)	19
36	13114.70	13114.34	13114.42	13115.31(30)	20
92	100616	100607	100614	100626(35)	21

^aDrake, Ref. 9

^bPlante *et al.*, Ref. 17.

4. Summary and Outlook

We have shown that the relativistic CI method with a complete, finite basis set is an effective way of treating the relativistic correlation energy problem. Extensions of these techniques to treat more complex many-electron ions are being developed. By moving the Hamiltonian matrix from the computer core to on-line hard disks, we can now run much bigger CI calculations on supercomputers as well as on fast workstations, limited only by the available disk space. For four-electron Be-like ions, we have carried out relativistic CI calculations with close to 35,000 configurations. The Hamiltonian matrix, even in symmetric storage mode (upper triangle only), takes up 5 GB of disk space and a single job can run for several days on an IBM RISC-6000 Model 580 workstation. Currently, we are looking into carrying out these calculations on massively parallel computers. CI calculations are ideally suited for distributed computing and parallel processing can speed them up by an order of magnitude easily. That will make it more practical to apply the relativistic CI method to complex atomic systems and pave the way for future large-scale, high-performance atomic structure calculations.

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