

Study of the importance of relativistic, correlation, and relaxation effects on ionization energy of atoms by a relativistic and correlated local density method

M. Vijayakumar and M. S. Gopinathan

Citation: *The Journal of Chemical Physics* **103**, 6576 (1995); doi: 10.1063/1.470385

View online: <http://dx.doi.org/10.1063/1.470385>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/103/15?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Model potential methods in atomic physics](#)

AIP Conf. Proc. **347**, 33 (1995); 10.1063/1.49190

[A modified parametrization scheme for the complete neglect of differential overlap method with relativistic correction of orbital exponents and energy levels with particular applications to rare earth compounds](#)

J. Chem. Phys. **96**, 4518 (1992); 10.1063/1.462813

[Interpretation of photoelectron spectra for ThF₄, UF₄, ThCl₄, and UCl₄ in terms of relativistic local density molecular orbital calculations](#)

J. Chem. Phys. **94**, 2928 (1991); 10.1063/1.459815

[Atomic physics in surface studies: An overview](#)

AIP Conf. Proc. **205**, 519 (1990); 10.1063/1.39220

[Relativistic linear combination of Gaussian type orbitals density functional method based on a two component formalism with external field projectors](#)

J. Chem. Phys. **92**, 1153 (1990); 10.1063/1.458177



Study of the importance of relativistic, correlation, and relaxation effects on ionization energy of atoms by a relativistic and correlated local density method

M. Vijayakumar

Department of Chemistry, Pondicherry University, Pondicherry-605 014, India

M. S. Gopinathan

Department of Chemistry, Indian Institute of Technology, Madras-600 036, India

(Received 18 April 1995; accepted 30 June 1995)

The effect of relativistic corrections, correlation, and relaxation on the ionization energy of inner and outer orbitals of light and heavy atoms has been studied using the “fully” correlated relativistic local density method—called the RC Ξ method. The validity of Koopmans’ theorem is also discussed in this paper. © 1995 American Institute of Physics.

INTRODUCTION

Electron spectroscopy for chemical analysis (ESCA) [x-ray photoelectron spectroscopy (XPS)]¹ has now been successfully used for probing the electronic structure of atoms, molecules, and solids. Electron ionization energies (IE) (or binding energies) of atoms and molecules can be directly measured from ESCA. It is known that the distribution of electron densities are considerably affected² by relativistic effects. The inner-shell electrons are more bound in the relativistic theory than in the nonrelativistic theory and hence the IEs become large for the former. Due to an indirect relativistic effect—the expansion of *d* and *f* orbitals—the relativistic outer shell *d* and *f* orbital electrons are more loosely bound than the nonrelativistic ones and so the IEs for the latter are large. These effects become more important for heavy atoms. Thus the ionization energy spectra are considerably affected by relativistic effects.

The calculation of ionization energy has been studied by *ab initio* methods^{2,3} and local-density methods.⁴ It is found^{5–9} that for an accurate calculation of inner-shell ionization energy, Breit interaction and quantum electrodynamics (QED) effects must be computed. Using the Dirac–Hartree–Fock–Slater method, Huang *et al.*⁹ have calculated the relaxed ionization energy with Breit interaction and QED corrections for atoms. Many authors^{3,10,11} discussed the importance of electron correlation in the calculation of atomic properties. In this paper, we have demonstrated the accuracy of our recently developed relativistic and correlated local density method (RC Ξ method)¹² by calculating the ionization energy and analyzing the importance of various effects. The RC Ξ ionization energies reported in this paper are corrected for Breit interaction and QED corrections which are taken from Ref. 9.

Under the assumption of Koopmans’ theorem,¹³ which states that the negative of the eigenvalue of the Hartree–Fock (HF) equation is equal to the ionization energy of an electron in that subshell ($IE_i = -\epsilon_i^{\text{HF}}$), the outer valence photoelectron spectra could be assigned. The success of this simple relation has been attributed¹⁴ to an error compensation between relaxation and correlation effects which are assumed to be similar in magnitude but opposite in sign. For

inner levels, the ionization energies obtained using this relation do not agree with the experimental results.¹⁵ A few methods^{15,16} have been proposed to correct Koopmans’ theorem for inner-shell ionization energies of atoms.

Migdalek and Bojara¹⁷ have studied the relative importance of the relativistic effects, the core polarization and relaxation in ionization potentials for Rb and Cs isoelectronic systems using the relativistic HF method. In their analysis, the effect of correlation on ionization potential is neglected.

In this paper, the relative magnitude and sign of these effects are studied for various atoms ($10 \leq Z \leq 80$). We have quantitatively estimated the *relaxation, correlation, and relativistic* corrections to the ionization energy of orbitals of these atoms using the RC Ξ method.¹² Using this information, we have analyzed the validity of Koopmans’ theorem for inner and valence orbitals of light, medium, and heavy atoms. The salient features of the RC Ξ method and the method of calculation are briefly discussed and this is followed by a discussion of the results.

THEORY OF THE RC Ξ METHOD AND THE METHOD OF CALCULATION

The RC Ξ method is a local-density formalism for atomic structure calculations that incorporates all the major relativistic corrections and Coulomb correlations.¹² The one-electron self-consistent-field (SCF) equation solved in the RC Ξ method is (in rydbergs)

$$[-\nabla^2 + v_i(r) + H_m(R) + H_D(r) + H_{so}(r)]u_i(r) = \epsilon_i u_i(r), \quad (1)$$

where $v_i(r)$ is the central-field potential for the *i*th spin orbital, $u_i(r)$ (where the subscript *i* represents the set of quantum numbers *n*, *l*, and *j* with *n* as the principal, *l* as the orbital angular momentum, and *j* as the total angular momentum quantum number of the *i*th spin orbital). $v_i(r)$ is given by

$$v_i(r) = -Z/r + v^C(r) + v_{\uparrow}^{\text{si}}(r) + v_{\uparrow}^{\text{ex}}(r) + v_{\uparrow}^{\text{corr}}(r). \quad (2)$$

Here, $v^C(r)$, the Coulombic electron–electron repulsion potential, is

$$v^c(r) = \sum_j n_j \int u_j^*(r') u_j(r') \frac{2}{|r-r'|} dr'. \quad (3)$$

$v_{\uparrow}^{\text{si}}(r)$, the self-interaction potential, is

$$v_{\uparrow}^{\text{si}}(r) = -n_i \int u_i^*(r') u_i(r') \frac{2}{|r-r'|} dr', \quad (4)$$

and $v_{i,\uparrow}^{\text{ex}}(r)$, the one-electron pure exchange potential, is defined as

$$v_{i,\uparrow}^{\text{ex}}(r) = -4\pi^{1/3} (2^{1/3} - 1) \left(\frac{1}{n_{\uparrow}} + \frac{1}{3} \right)^{-2/3} \\ \times \left[2\rho_{i,\uparrow}(r) \rho_{\uparrow}^{-2/3}(r) - \frac{2}{3} \rho_{\uparrow}^{-5/3}(r) \sum_{i,\uparrow} n_i u_i^*(r) u_i(r) \right. \\ \left. \times (\rho_{\uparrow}(r) - \rho_{i,\uparrow}(r)) \right]. \quad (5)$$

Here, $\rho_{i,\uparrow}(r)$ is the electron density of up-spin electrons in the i th spin orbital, defined as

$$\rho_{i,\uparrow}(r) = n_{i,\uparrow} u_{i,\uparrow}^*(r) u_{i,\uparrow}(r),$$

$\rho_{\uparrow}(r)$, the electron density of all up-spin electrons, is

$$\rho_{\uparrow}(r) = \sum_{i,\uparrow} n_i u_i^*(r) u_i(r),$$

$\rho(r)$, the total electron density of the system, is

$$\rho(r) = \rho_{\uparrow}(r) + \rho_{\downarrow}(r),$$

and $v_{\uparrow}^{\text{corr}}(r)$, the correlation potential acting upon the up-spin electron at point r due to down-spin electrons, is

$$v_{\uparrow}^{\text{corr}}(r) = -\frac{4\pi}{27} \rho_{\downarrow}(r) \left(\frac{(r_c^3)_{\uparrow}}{1+(r_c)_{\uparrow}} + \frac{(r_c^3)_{\downarrow}}{1+(r_c)_{\downarrow}} \right) \\ + \frac{3}{81} \pi^{2/3} \left(\frac{1}{n_{\downarrow}} + \frac{1}{3} \right)^{-1/3} \rho_{\uparrow}^{-1/3}(r) \rho_{\downarrow}(r) \\ \times \left(\frac{[3(r_c^2)_{\downarrow} + 2(r_c^3)_{\downarrow}]}{[1+(r_c)_{\downarrow}]^2} \right). \quad (6)$$

Here $(r_c)_{\uparrow}$ is the “radius” of the Coulomb hole and is given by

$$(r_c)_{\uparrow} = \frac{3}{4} \left[\left(\frac{1}{n_{\downarrow}} + \frac{1}{3} \right) \pi \rho_{\uparrow}(r) \right]^{-1/3}. \quad (7)$$

So far, we have defined the various terms in the central field potential $V_i(r)$ in Eq. (1). We now define the relativistic terms in Eq. (1). The term $H_m(r)$ the mass-velocity correction is given by

$$H_m(r) = -\frac{\alpha^2}{4} [\epsilon_i - v_i(r)]^2. \quad (8)$$

$H_D(r)$ is the Darwin correction:

$$H_D(r) = -\frac{\alpha^2 B}{4} \frac{dv_i(r)}{dr} \left(\frac{d}{dr} - \frac{1}{r} \right), \quad (9)$$

and $H_{so}(r)$ is the spin-orbit interaction term

TABLE I. Comparison of orbital ionization energies (in Ry) for Ne, Kr, and Hg atoms calculated by the present method with and without relativistic effects.

Atom	Orbital ^a	IE Ξ ^b	IE $\text{RC}\Xi$ ^{c,d}	IE DHFS ^e	IE expt ^f
Ne	1s ₊	63.831	63.982	63.881	63.962
	2s ₊	3.610	3.699	3.616	3.559
	2p ₋		1.529	1.433	1.592
		1.522			
Kr	2p ₊		1.519	1.426	1.585
	1s ₊	1036.124	1052.857	1052.920	1052.940
	2s ₊	137.542	141.923	141.900	141.460
	2p ₋		127.520	127.280	127.220
		123.562			
	2p ₊		123.456	123.400	123.360
	3s ₊	20.701	21.751	21.740	21.520
	3p ₋		16.638	16.524	16.332
		15.644			
	3p ₊		16.049	15.936	15.758
3d ₋		6.951	6.858	6.976	
	6.796				
	3d ₊		6.856	6.766	6.888
	4s ₊	2.257	2.445	2.264	2.014
	4p ₋		1.179	1.040	1.067
		1.039			
Hg	4p ₊		1.023	0.954	1.030
	1s ₊	5548.502	6112.723	6107.760	6108.380
	2s ₊	935.638	1092.959	1092.000	1091.020
	2p ₋		1047.702	1044.700	1044.680
		897.634			
	2p ₊		904.152	903.280	903.200
	3s ₊	222.775	264.457	263.400	262.120
	⋮	⋮	⋮	⋮	⋮
	4f ₋		8.341	7.984	7.860
		8.393	(8.119)	(7.814)	(7.700)
	4f ₊		7.951	7.686	7.580
	5d ₋		1.200	1.104	1.228
		1.286	(1.116)	(1.027)	(1.145)
5d ₊		1.060	0.975	1.090	
6s ₊	0.480	0.738	0.632	0.768	

^aNote that the symbol (+) means $j=l+1/2$ and the symbol (-) means $j=l-1/2$.

^bThe nonrelativistic values are calculated using the nonrelativistic Ξ method (Ref. 22).

^cThe relativistic values are calculated using the present relativistic method and are corrected with the Breit interaction and QED effects which are taken from Ref. 9.

^dThe values in the parenthesis represent the weighted average of the ionization energies with J_+ and J_- .

^eThe DHFS values which are corrected for Breit interaction and QED effects are taken from Ref. 9.

^fThe experimental values are taken from Ref. 23.

$$H_{so}(r) = -\frac{\alpha^2 B}{4} \Lambda \frac{dv_i(r)}{dr} \frac{1}{r} \quad (10)$$

with α the fine structure constant,

$$B = \left[1 + \frac{\alpha^2}{4} (\epsilon_i - v_i(r)) \right]^{-1},$$

$\Lambda = l+1$ for $j=l+1/2$ and $\Lambda = -l$ for $j=l-1/2$.

The $v_i(r)$ present in the above relativistic terms is defined in Eq. (2). The important features of the $\text{RC}\Xi$ formalism are the following (Ref. 12 may be consulted for further details).

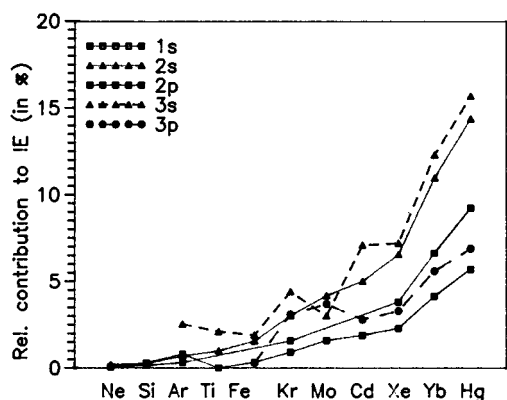


FIG. 1. The percentage of relativistic correction to ionization energy of various orbitals of light, medium and heavy atoms.

- (1) It is a single component quasirelativistic method with the spin-orbit interaction included in the Hamiltonian.
- (2) The two type of correlations namely Fermi exchange and Coulomb correlation are treated separately so that all important distinct properties of the Fermi and Coulomb holes are satisfied.
- (3) Local density formalism is employed so that the numerical solution of Eq. (1) is as simple as that of the standard Herman-Skillman program.¹⁸ The calculation requires only a few minutes on a PC/AT machine even for large atoms.
- (4) The present method distinguishes between the spin-orbit levels and this makes the wave function $u_i(r)$ dependent on the quantum number j .
- (5) The finite nuclear size correction is ignored in this model.

We now present the method of calculation of the IE. Theoretically, the orbital ionization energy may be calculated either by (i) the Δ SCF procedure¹⁹ or (ii) the Slater's transition state procedure.²⁰ In the Δ SCF procedure, the IE of the i th orbital is equal to the energy difference between the average total energies of the atom $E^{\text{tot}}(A)$ and its ion $E_i^{\text{tot}}(A^+)$ where one electron has been removed from the i th orbital and is given as

$$\text{IE}_i = E_i^{\text{tot}}(A^+) - E^{\text{tot}}(A). \quad (11)$$

The total energy has been calculated as the sum of correlation energy and the total energy for $\text{RC}\Xi$ one-electron wave functions [from Eq. (1)] with Hartree-Fock Hamiltonian.

In the transition state procedure, the ionization energy of the i th orbital is equal to the negative of the eigenvalue of the corresponding orbital where one-half of the electron in the i th orbital has been removed. It has been shown²¹ that the relaxation of the core orbitals upon ionization is not fully taken care of in the transition state method. We have used the Δ SCF procedure to calculate the orbital IEs from the average total energies calculated by the $\text{RC}\Xi$ method.

RESULTS

In Table I, we give the results for typical light (Ne), medium heavy (Kr), and heavy (Hg) atoms. In column three

of Table I, the nonrelativistic IEs are given which are calculated using the nonrelativistic Ξ method.²² The nonrelativistic Ξ values are obtained by setting to zero the relativistic terms $H_m(r)$, $H_D(r)$, and $H_{so}(r)$ in Eq. (1). For a light atom such as Ne, the nonrelativistic and relativistic values agree well with the experimental results²³ for core orbitals; but for Kr the $\text{RC}\Xi$ values are closer to the experimental results than those of the nonrelativistic Ξ values. This clearly shows the importance of relativistic corrections to the IEs even for medium atoms. For heavy atoms, the error due to the neglect of relativistic effects becomes large. The large change in the ionization energy of core orbitals on going from Ξ to $\text{RC}\Xi$ is due to the relativistic contraction of these orbitals. Due to indirect relativistic effects, the outer d and f orbitals will expand resulting in the decrease of their ionization energies.

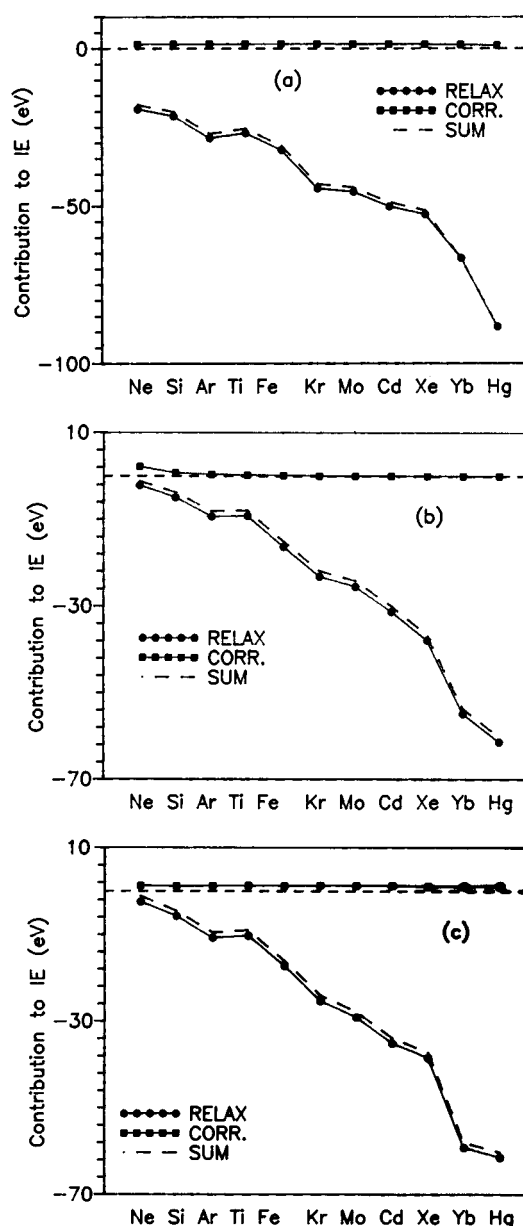


FIG. 2. The contribution of relaxation energy, correlation energy and the sum of these two energies to ionization energy of (a) 1s orbital, (b) 2s orbital, and (c) 2p orbital.

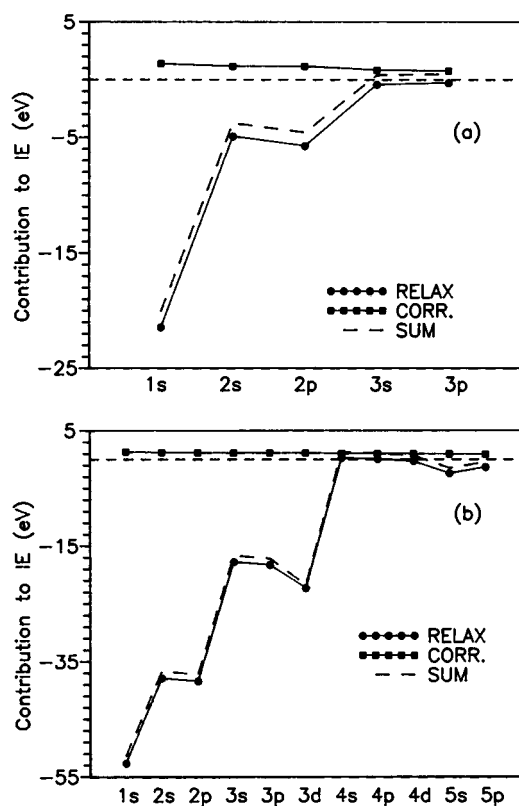


FIG. 3. The contribution of relaxation energy, correlation energy and the sum of these two energies to ionization energy of orbitals of (a) Si and (b) Xe.

This is clearly indicated in Table I where the ionization energies of $4f$ and $5d$ orbitals of Hg calculated by the relativistic method (RC Ξ) are small compared to IEs calculated by the nonrelativistic Ξ method.

An orbital-wise analysis of the relativistic correction to the ionization energies of orbitals such as $1s$, $2s$, $2p$, $3s$, and $3p$ of various atoms is shown in Fig. 1. The relativistic contribution to ionization energy from each orbital in a heavy atom is considerable being in the range of 5%–10%. The relativistic contribution to ionization energy of orbital $2s$ is more than that of $2p$ orbital.

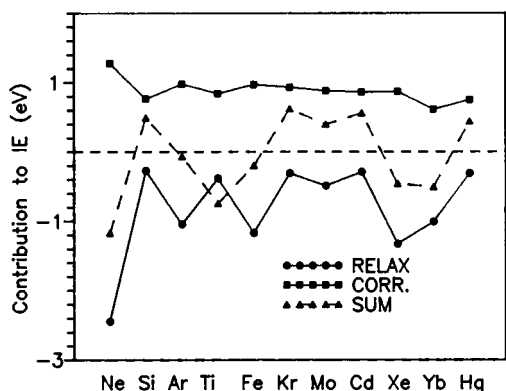


FIG. 4. The contribution of relaxation energy, correlation energy and the sum of these two energies to the valence orbital ionization energy of various atoms.

We now discuss the effect of relaxation and correlation on ionization energy and analyze the validity of Koopmans' theorem

$$\Delta E_i^{\text{corr}} = E_i^{\text{corr}}(A^+) - E_i^{\text{corr}}(A). \quad (12)$$

The contribution of correlation energy (ΔE_i^{corr}) to ionization energy is calculated as the difference in the total correlated energy of the ion and the atom obtained from the RC Ξ method. The relaxation energy ($\Delta E_i^{\text{relax}}$) is calculated using the following expression:

$$\Delta E_i^{\text{relax}} = \text{IE}_i + \epsilon_i, \quad (13)$$

where IE_i represents the ionization energy of the i th orbital and ϵ_i is the eigenvalue of the i th orbital in the RC Ξ method. Calculations of the correlation effect (ΔE_i^{corr}) and of the relaxation effect ($\Delta E_i^{\text{relax}}$) have been performed for inner orbitals such as $1s$, $2s$, and $2p$ orbitals of light, medium, and heavy atoms. The results are shown in Figs. 2(a)–2(c), and for orbitals within the atom Si and Xe, the results are shown in Figs. 3(a) and 3(b). In all these figures, the sum of these two energies is also shown. It is seen from Figs. 2(a)–2(c) that the correlation contribution to the IE is almost a constant for these inner shells. But the relaxation energy increases with the atomic number and it is very large in magnitude compared with the correlation energy for inner shells. In the case of orbitals within a given atom, the relaxation energy is more for inner orbitals than those for the outer orbitals [Figs. 3(a) and 3(b)].

Figures 2(a)–2(c) clearly show that the sum of correlation and relaxation effects is never small for inner orbitals. Hence, it follows that the Koopmans' theorem is not strictly valid for inner shells even for small atoms like Ne. It is seen that the Breit interaction and QED effects dominate³ correlation for inner-shell ionization.

The contribution of relaxation energy and of correlation energy to IE of valence orbitals or these atoms and their sum are shown in Fig. 4. It is seen that these two effects do not exactly cancel each other. However, the net sum ranges from -1.2 to 0.6 eV. So within the experimental error, it is reasonable to assign the valence peaks in photoemission electron spectroscopy using the orbital eigenvalues. On the contrary to inner-shell ionization, correlation is important for valence-shell ionization compared to Breit interaction and QED effects. In conclusion, we can state that the Koopmans' approximation is valid only for valence orbitals and not strictly valid for inner orbitals of any atom.

CONCLUSION

Using the relativistic and correlated RC Ξ method, the relative importance of relativistic, correlation, and relaxation effects on ionization energies is studied. It is found from this study, that the correlation contribution to ionization energy is the same for inner as well as outer orbitals and the relaxation effect dominates over the correlation effect. Since there is no exact cancellation between them, the Koopmans' theorem does not strictly hold for inner orbitals. However, for outer

orbitals, these two effects are almost equal in magnitude and thus cancel each other; so Koopmans' theorem may be used for the outer orbitals.

- ¹K. Siegbahn *et al.*, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969); T. A. Carlson, *Photoelectron and Auger Spectroscopy* (Plenum, New York, 1975).
- ²*Relativistic Effects in Atoms, Molecules, and Solids*, Series B; Physics Vol. 87, edited by G. L. Malli, NATO ASI Series (Plenum, New York, 1983).
- ³J. Simons and K. D. Jordan, *Chem. Rev.* **87**, 535 (1987); Y.-K. Kim, *Phys. Scr.* **T47**, 54 (1993).
- ⁴*Local Density Approximations in Quantum Chemistry and Solid State Physics*, edited by J. P. Dahl and J. Avery (Plenum, New York, 1984).
- ⁵A. Rosen and I. Lindgren, *Phys. Rev.* **176**, 114 (1968).
- ⁶A. M. Desiderio and W. R. Johnson, *Phys. Rev. A* **3**, 1267 (1971).
- ⁷J. B. Mann and W. R. Johnson, *Phys. Rev. A* **4**, 41 (1971).
- ⁸J. P. Desclaux, *At. Data Nucl. Data Tables* **12**, 311 (1973).
- ⁹H. N. Huang, M. Aoyagi, M. H. Chen, B. Crasemann, and H. Mark, *At. Data Nucl. Data Tables* **18**, 243 (1976).
- ¹⁰P. B. Ivanov and U. I. Safronova, *Phys. Scr.* **49**, 408 (1994); U. I. Safronova, M. S. Safronova, and R. Bruch, *ibid.* **49**, 446 (1994).
- ¹¹T. Brage and C. F. Fischer, *Phys. Scr.* **T47**, 18 (1993).
- ¹²M. Vijayakumar, N. Vaidehi, and M. S. Gopinathan, *Phys. Rev. A* **40**, 6834 (1989).
- ¹³T. Koopmans, *Physica* **1**, 104 (1933).
- ¹⁴K. Schwartz, *J. Phys. B: At. Mol. Phys.* **11**, 1339 (1978).
- ¹⁵R. Manne and T. Aberg, *Chem. Phys. Lett.* **7**, 282 (1970).
- ¹⁶Y. Tal and J. Katriel, *Phys. Lett. A* **61**, 288 (1977).
- ¹⁷J. Migdalek and A. Bojara, *J. Phys. B: At. Mol. Phys.* **17**, 1943 (1984).
- ¹⁸F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, New York, 1963).
- ¹⁹P. S. Bagus, *Phys. Rev.* **139**, A619 (1965).
- ²⁰J. C. Slater, *Int. J. Quantum Chem. Symp.* **3**, 727 (1970); J. C. Slater and J. H. Wood, *ibid.* **4**, 3 (1971).
- ²¹V. Selvaraj and M. S. Gopinathan, *J. Phys. B: At. Mol. Phys.* **18**, 3043 (1985).
- ²²N. Vaidehi and M. S. Gopinathan, *Phys. Rev. A* **29**, 1679 (1989).
- ²³*CRC Handbook of Chemistry and Physics*, 68th ed., 1987–1988 (Chemical Rubber, Boca Raton, 1987); J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.* **39**, 125 (1967).