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Transition energies of ytterbium, lutetium, and lawrencium by the relativistic coupled-cluster method

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The relativistic Fock-space coupled-cluster method was applied to the Yb, Lu, and Lr atoms, and to several of their ions. A large number of transition energies was calculated for these systems. Starting from an all-electron Dirac-Fock or Dirac-Fock-Breit function, many electrons (30–40) were correlated to account for core-valence polarization. High-l virtual orbitals were included (up to $l = 5$) to describe dynamic correlation. Comparison with experiment (when available) shows agreement within a few hundred wave numbers in most cases. Fine-structure splittings are even more accurate, within 30 cm^{-1} of experiment. Average errors are at least three times smaller than for previous calculations. Two bound states of Lu$^-$ are predicted, $6p5d\,^1D_2$ and $6p^2\,^3P_0$, with binding energies of about 2100 and 750 cm^{-1}, respectively. The ground state of lawrencium is $^2P_{1/2}$, relativistically stabilized relative to $^2D_{3/2}$, the ground state of Lu. Two states of the Lr$^-$ anion are bound, $7p^2\,^3P_0$ (by 2500 cm^{-1}) and $7p6d\,^1D_2$ (by 1300 cm^{-1}).

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I. INTRODUCTION

Transition energies (ionization potentials, excitation energies, and electron affinities) are experimentally known for most atoms, including many of the lanthanides [1]. This information is more scarce for the actinides, in particular for the transuranium elements. The development of reliable high-precision *ab initio* methods for the theoretical investigation of these systems is therefore highly desirable. Such methods must treat simultaneously relativistic and correlation effects, since both play an important role in the spectra of heavy elements.

The multiconfiguration Dirac-Fock (MCDF) method has been applied to a number of atomic systems over the past 20 years (see, e.g., [2–7]). Relativity is included by using the Dirac Hamiltonian, and the large number of configurations in the MCDF function (on the order of several hundred) takes care of some correlation effects, particularly those due to quasidegeneracies (nondynamic correlation). Dynamic correlation, which requires many more configurations and high-l virtual orbitals for proper description, is not represented satisfactorily, leading to errors in some cases. Thus it has been recently shown [8] that dynamic correlation reverses the order of the two lowest states of rutherfordium, leading to a $6d^2$ ground state rather than the $6d7p$ predicted by MCDF.

The past few years have seen an intensive development of relativistic many-body techniques in atomic physics and quantum chemistry, in particular the method of fully relativistic (Dirac-equation based) coupled-cluster (RCC) theory [9–20]. The coupled cluster is an all-order method and yields upon iteration the order-by-order many-body perturbation theory (MBPT). Infinite subclasses of perturbation diagrams are summed and size extensivity is maintained. The latter feature is particularly important for heavy elements, which are also elements where relativistic effects are most significant. An additional advantage of the coupled-cluster (CC) approach is connected with the similarity of CC and MBPT expansion terms. Using this property one can, if necessary, improve the CC results by adding the most important omitted diagrams with the aid of low-order MBPT. The RCC method gives both electron correlation and relativistic effects with high accuracy and is a powerful and systematic method for calculating properties of heavy atomic and molecular systems.

The implementation of relativistic CC may be done either numerically [10] or by using discrete basis sets, which may be local [11,12] or global [13–20]. We have recently developed and implemented a relativistic version of the multireference valence-universal Fock-space coupled-cluster method, using a discrete basis of four-component Gaussian spinors (G spinors), which may also be applied to molecular systems. The method is based on the Dirac-Coulomb-Breit (DCB) Hamiltonian and incorporates the instantaneous Coulomb and low-frequency Breit interactions to all orders. Accurate ionization potentials, excitation energies, and fine-structure splittings were obtained for Au [15], highly ionized atoms with two to five electrons [16], and the alkali-metal atoms Li to Fr [17]. Pair correlation energies were calculated for all the electron pairs of the Xe atom [18] and, more recently, energy levels of Pr^{3+} and U^{4+} were calculated [19] and ground-state electron configurations were determined for elements 104 [8] and 111 [20].

Previous applications to lanthanides and actinides involved the f^2 electron configuration [19]. Here we apply the RCC method to atoms near the end of the f

series, the lanthanides Yb and Lu and the actinide Lr. MCDF calculations on some states of Yb and Yb^+ have been reported by Migdalek and co-workers [21,22] and by Kotochigova and Tupizin [23], with the former including core polarization via core-polarization potentials or second-order perturbation theory. Migdalek and Baylis also calculated Lu^+ [24], while Vosko *et al.* applied the density-functional theory (DFT) to Lu and Lu^- [25,26]. Lu and Lr were investigated by Desclaux and Fricke [3] using MCDF.

II. METHOD

The relativistic coupled-cluster method has been described in our previous publications [15,17], and only a brief review is given here. We start from the projected Dirac-Coulomb (or Dirac-Coulomb-Breit) Hamiltonian advocated by Sucher [27]

$$H_+ = H_0 + V, \tag{1}$$

where (in atomic units)

$$H_0 = \sum_i \Lambda_i^+ h_D(i) \Lambda_i^+, \tag{2}$$

$$h_D(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2(\beta_i - 1) + V_{\mathrm{nuc}}(i) + U(i), \tag{3}$$

$$V = \sum_{i<j} \Lambda_i^+ \Lambda_j^+ (V_{\mathrm{eff}})_{ij} \Lambda_j^+ \Lambda_i^+ - \sum_i \Lambda_i^+ U(i) \Lambda_i^+. \tag{4}$$

Here h_D is the one-electron Dirac Hamiltonian. An arbitrary potential U is included in the unperturbed Hamiltonian H_0 and subtracted from the perturbation V. This potential is chosen to approximate the effect of the electron-electron interaction; in particular, it may be the Dirac-Fock self-consistent-field potential. The nuclear potential V_{nuc} includes the effect of finite nuclear size. Λ_i^+ are projection operators onto the positive energy states of the Dirac Hamiltonian h_D. Because of their presence, the Hamiltonian H_+ has normalizable, bound-state solutions. This approximation is known as the no-(virtual)-pair approximation, since virtual electron-positron pairs are not allowed in intermediate states. The form of the effective potential V_{eff} depends on the gauge used. In Coulomb gauge it becomes (in atomic units, correct to second order in the fine-structure constant α) [9]

$$V_{\mathrm{eff}} = \frac{1}{r_{12}} + B_{12} + O(\alpha^3), \tag{5}$$

where the frequency-independent Breit interaction is

$$B_{12} = -\frac{1}{2r_{12}} [\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + (\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})/r_{12}^2]. \tag{6}$$

In q-number theory the Dirac-Coulomb-Breit Hamiltonian H_+ is rewritten in terms of normal-ordered products of the spinor operators $\{r^+s\}$ and $\{r^+s^+ut\}$ [27,28]

$$\begin{aligned} H &= H_+ - \langle 0|H_+|0\rangle \\ &= \sum_{r,s} f_{rs}\{r^+s\} + \frac{1}{4}\sum_{r,s,t,u} \langle rs||tu\rangle \{r^+s^+ut\}, \end{aligned} \tag{7}$$

where f_{rs} and $\langle rs||tu\rangle$ are, respectively, elements of one-electron Dirac-Fock and antisymmetrized two-electron Coulomb-Breit interaction matrices over Dirac four-component spinors. The effect of the projection operators Λ^+ is now taken over by the normal ordering, denoted by the curly brackets in the equation above, which requires annihilation operators to be moved to the right of creation operators as if all anticommutation relations vanish. The Fermi level is set at the top of the highest occupied positive energy state and the negative energy states are ignored.

The no-pair approximation leads to a natural and straightforward extension of the nonrelativistic open-shell CC theory. The multireference valence-universal Fock space coupled-cluster approach is employed here, which defines and calculates an effective Hamiltonian in a low-dimensional model (or P) space, with eigenvalues approximating some desirable eigenvalues of the physical Hamiltonian. According to Lindgren's formulation of the open-shell CC method [29], the effective Hamiltonian has the form

$$H_{\mathrm{eff}} = PH\Omega P, \tag{8}$$

where Ω is the normal-ordered wave operator

$$\Omega = \{\exp(S)\}. \tag{9}$$

The excitation operator S is defined in the Fock-space coupled-cluster approach with respect to a closed-shell reference determinant. In addition to the traditional decomposition into terms with different total (l) number of excited electrons, S is partitioned according to the number of valence holes (m) and valence particles (n) to be excited with respect to the reference determinant,

$$S = \sum_{m\geq 0}\sum_{n\geq 0}\left(\sum_{l\geq m+n} S_l^{(m,n)}\right). \tag{10}$$

The upper indices in the excitation amplitudes reflect the partitioning of the Fock space into sectors, which correspond to the different numbers of electrons in the physical system. This partitioning allows for partial decoupling of the open-shell CC equations. The equations for the (m,n) sector involve only S elements from sectors (k,l) with $k \leq m$ and $l \leq n$, so that the very large system of coupled nonlinear equations is separated into smaller subsystems, which are solved consecutively: First, the equations for $S^{(0,0)}$ (corresponding to the reference determinant) are iterated to convergence; the $S^{(1,0)}$ (or $S^{(0,1)}$) equations are then solved using the known $S^{(0,0)}$, and so on. This separation, which does not involve any approximation, reduces the computational effort significantly. The eigenvalues of the effective Hamiltonian (8) in a sector give directly the correlated energies in that sector with respect to the correlated (0,0) reference state. These transition energies may be ionization potentials, electron affinities, or excitation energies, according to the presence of valence holes and/or valence particles.

In the present application, we use the (0,0), (0,1), and (0,2) sectors. The lower index l in (10) is truncated at l=2. The resulting coupled cluster with single and double excitations (CCSD) scheme involves the fully self-consistent, iterative calculation of all one- and two-body virtual excitation amplitudes and sums all diagrams with these excitations to infinite order. Negative energy states are excluded from the Q space and the diagrammatic summations in the CC equations are carried out only within the subspace of the positive energy branch of the Dirac-Fock spectrum.

III. CALCULATIONS

The Fock-space relativistic coupled-cluster method was applied to the Yb, Lu, and Lr atoms, in several ionization states. The Dirac-Fock-Coulomb or Dirac-Fock-Breit equations were solved for the closed-shell systems Yb^{+2}, Lu^{+3}, Lu^{+}, and Lr^{+}, which define the (0,0) sector in each case. These systems were correlated by CCSD and two electrons were then added, one at a time, to reach the desired states of Yb^{+}, Yb, Lu^{+2}, Lu^{+}, Lu, Lu^{-}, Lr, and Lr^{-}.

The Dirac-Fock [28] and RCC [15,17] programs are both written for spherical symmetry, utilizing the angular decomposition of the wave function and CC equations in a central field. The energy integrals and CC amplitudes that appear in the Goldstone-type diagrams defining the CC equations are decomposed in terms of vector-coupling coefficients, expressed by angular-momentum diagrams, and reduced Coulomb-Breit or S matrix elements, respectively. The reduced equations for single and double excitation amplitudes are derived using the Jucys-Levinson-Vanagas theorem [29] and solved iteratively. This technique makes possible the use of larger basis sets.

To avoid "variational collapse" [30], the Gaussian spinors in the basis are made to satisfy kinetic balance [31]. They also satisfy relativistic boundary conditions associated with a finite nucleus, described here as a sphere of uniform proton charge [28]. The atomic masses used are 173.939 for Yb, 174.97 for Lu, and 257 for Lr. The speed of light c is 137.0599 a.u.

The uncontracted well-tempered basis set of Huzinaga and Klobukowski [32] was used for Yb and the universal basis set of Malli *et al.* [33] was selected for Lu and Lr. The basis sets, which go up to h orbitals ($l = 5$), are summarized in Table I. Atomic orbitals with the same l but different k number (e.g., $p_{1/2}$ and $p_{3/2}$) are expanded in the same basis functions. To include core-valence polarization effects, a large number of electrons are correlated. Thus only the Kr electrons are treated as core in the RCC calculation of Yb and Lu (*all* orbitals are optimized at the Dirac-Fock stage), so that the $4df5spd6sp$ electrons are correlated. For Lr, $\mathrm{Xe}(4f^{14})$ defines the core and the $5df6spd7sp$ electrons are correlated. The virtual orbitals with high orbital energies have been found to contribute very little to correlation effects on excitation energies; orbitals higher than 100 a.u. are therefore eliminated from the calculation, effecting considerable savings in computational effort. All computations were carried out on the IBM RS6000/360 computer workstation at Tel Aviv University.

IV. RESULTS AND DISCUSSION

A. Ytterbium

Starting from the closed-shell configuration $4f^{14}$ of Yb^{+2}, two electrons were added (one at a time) in the $5d$, $6s$, and $6p$ orbitals. The ionization potential (IP) and excitation energies (EE's) of Yb^{+} are shown in Table II. They are compared with experiment [1] and previous calculations [22]. The agreement of our results with experiment is very good, with an average error of 644 cm^{-1} and a maximum error of 920 cm^{-1}. As found earlier [19], the Breit interaction has a small effect. The Dirac-Fock function corrected by perturbation or core-polarization potentials [22] yields much larger errors. Good agreement with experiment is also found for the levels of neutral Yb (Table III). Excitation energies are correct within a few hundred wave numbers, with the exception of the two high singlet states. The fine-structure splittings are highly accurate, with the largest error in the DCB results smaller than 30 cm^{-1}.

B. Lutetium

Two sets of calculations were performed for Lu. The first started from the $4f^{14}6s^2$ configuration of Lu^{+}; adding up to two electrons in the $5d$ and $6p$ shells gives the ionization potential, low-energy excitations, and electron affinities of the atom. Good agreement with experiment is obtained for the IP and EE's (Table IV). Fine-structure splittings are again highly accurate. The CCSD electron affinities, which have not been measured, differ considerably from the DFT results of Vosko *et al.*

TABLE I. Basis sets for Yb, Lu, and Lr. Members of the well-tempered s-basis series used in the various l sectors are given.

Atom	Basis	Ref.	s	p	d	f	g	h
Yb	$31s26p21d15f10g6h$	[32]	1–31	5–30	8–28	13–27	16–25	19–24
Lu	$34s25p20d15f10g6h$	[33]	1–34	9–33	13–32	17–31	21–30	24–29
Lr	$34s25p21d15f10g6h$	[33]	1–34	9–33	13–33	17–31	21–30	24–29

TABLE II. Ionization potential (IP) and excitation energies (EE's) of Yb^+ (cm^{-1}). DF plus PT, Dirac-Fock corrected by second-order perturbation theory [22]; DF plus CP, Dirac-Fock plus core polarization [22]; DC, relativistic coupled cluster, starting from the Dirac-Coulomb Hamiltonian, DCB, relativistic coupled cluster starting from the Dirac-Coulomb-Breit Hamiltonian. The experimental results are from Ref. [1].

			Present work		Other results	
Quantity	State	Expt.	DC	DCB	DF plus PT	DF plus CP
IP	$6s$	98269	97934	97876	102764	95317
EE	$5d_{3/2}$	23285	23770	23720	28210	20333
	$5d_{5/2}$	24333	25072	24998	28792	21140
	$6p_{1/2}$	27062	27868	27870	30834	26559
	$6p_{3/2}$	30392	31324	31312	33962	29679
Average error			659	644	4244	2063

TABLE III. Ionization potential, excitation energies, and fine-structure splittings (FS's) of Yb (cm^{-1}). MCDF, multiconfiguration Dirac-Fock method [23]; +CP MCDF with core polarization added [21]. The other definitions are the same as in Table II. The experimental results are from Ref. [1].

			Present work		Other results	
Quantity	State or splitting	Expt.	DC	DCB	MCDF	+CP
IP	$6s^2\ {}^1S_0$	50441	51143	51109		48074
EE	$6s6p\ {}^3P_0$	17288	17346	17359	15829	
	${}^3P_1$	17992	18082	18089	16563	
	${}^3P_2$	19710	19847	19836	18167	
	$5d6s\ {}^3D_1$	24489	24981	24936		
	${}^3D_2$	24752	25229	25180		
	${}^3D_3$	25271	25735	25676		
	$6s6p\ {}^1P_1$	25068	27283	27271	27838	23120
	$5d6s\ {}^1D_2$	27678	28673	28587		
Average error			626	595	1800	
FS	${}^3P_1$-${}^3P_0$	704	736	730	734	
	${}^3P_2$-${}^3P_1$	1718	1765	1747	1604	
	${}^3D_2$-${}^3D_1$	263	248	244		
	${}^3D_3$-${}^3D_2$	519	506	496		

TABLE IV. Ionization potential, excitation energies, and electron affinities (EA's) of Lu (cm^{-1}). MCDF, multiconfiguration Dirac-Fock method [3], DFT, density functional theory (the different values given use different density functionals) [25,26]; DC, relativistic coupled cluster with the Dirac-Coulomb Hamiltonian (present work). The experimental results are from Ref. [1].

Quantity	State	Expt.	DC	MCDF	DFT		
IP	$5d6s^2\ {}^2D_{3/2}$	43762	42757		44504	42858	
EE	$2D_{5/2}$	1994	1975		1580	1536	
	$6s^26p\ {}^2P_{1/2}$	4136	3828	~1000	3862	3094	
	${}^2P_{3/2}$	7476	7140				
EA	$6s^26p5d\ {}^1D_2$		2076		4499	4258	2173
	$6s^26p^2\ {}^3P_0$		746				
	$6s^26p5d\ {}^3D_2$		−336				
	${}^3D^{\mathrm{a}}$		−1014		3665	3556	
	${}^3F_4$		−2628				
	${}^3F^{\mathrm{a}}$		−3304		2129	2239	2327

[a] LS term average.

TABLE V. Ionization potentials and excitation energies of Lu^+ and Lu^{2+} (cm^{-1}). DC, relativistic coupled cluster with the Dirac-Coulomb Hamiltonian (present work); Other, MCDF plus core polarization for Lu^+ [24], and Dirac-Fock plus second-order perturbation for Lu^{2+} [22]. The experimental results are from Ref. [1].

Quantity	State	Expt.	DC	Other
		Lu^+		
IP	$6s^2\ {}^1S_0$	112000±3000	113914	110534
EE	$5d6s\ {}^3D_1$	11796	12861	
	${}^3D_2$	12435	13500	
	${}^3D_3$	14199	15253	
	${}^1D_2$	17333	18538	
	$6s6p\ {}^3P_0$	27264	27569	
	${}^3P_1$	28503	28821	27984
	${}^3P_2$	32453	32811	
	${}^1P_1$	38223	38965	36970
Average error		764		
		Lu^{2+}		
IP	$6s\ {}^2S_{1/2}$	169049	169135	172002
EE	$5d\ {}^2D_{3/2}$	5708	6812	7785
	${}^2D_{5/2}$	8648	9767	10332
	$6p\ {}^2P_{1/2}$	38401	38688	40154
	${}^2P_{3/2}$	44705	44998	45864
Average error			578	1925

[25,26]. In agreement with two of the three density functionals used by them, we predict a $6s^26p5d\ {}^1D_2$ ground state for the anion, but our electron affinity is one-half of theirs. Another weakly bound state of the anion is the $6s^26p^2\ {}^3P_0$, not considered by Vosko *et al.* On the other hand, we do not get electron binding in the ${}^3D$ and the ${}^3F$ states, although the former may be weakly bound.

A second set of calculations started from the $4f^{14}$ configuration of Lu^{+3}, isoelectronic with Yb^{+2} considered in the preceding subsection. Adding one or two electrons in the $6s$, the $6p$, and the $5d$ orbitals yields the ionization potentials and excitation energies of Lu^+ and Lu^{+2} (Table V). Satisfactory agreement with experiment [1] is obtained and the RCC results are significantly better than MCDF values [24]. The states involving a $5d$ electron are ~1000 cm^{-1} too high, probably due to remaining deficiencies in the basis.

C. Lawrencium

Here we start from the $5f^{14}7s^2$ configuration of Lr^+ and add up to two electrons in the $6d$ and the $7p$ orbitals (Table VI). While Lu has a $5d$ ground state, relativistic stabilization of the $7p_{1/2}$ orbital relative to the $6d$ in the heavier Lr is sufficient to have a $7p_{1/2}$ ground state, with the $6d_{3/2}$ state about 1300 cm^{-1} higher. This order was also found by Desclaux and Fricke [3] using MCDF. Their calculated $6d_{3/2}$ excitation energy was 3600 cm^{-1}, but they extrapolated MCDF errors in lighter atoms and quoted 1500±1000 cm^{-1} for this energy, close to our *ab initio* result.

TABLE VI. Ionization potential, excitation energies, and electron affinities of Lr (cm^{-1}). MCDF, multiconfiguration Dirac-Fock [3], DC, relativistic coupled cluster, with the Dirac-Coulomb Hamiltonian, DCB, RCC with the Dirac-Coulomb-Breit Hamiltonian.

	State	Present work		
Quantity		DC	DCB	MCDF
IP	$7s^27p_{1/2}\,{}^2P_{1/2}$	39511	39419	
EE	$7s^26d_{3/2}\,{}^2D_{3/2}$	1388	1263	1500±1000[a]
	$7s^26d_{5/2}\,{}^2D_{5/2}$	5236	5062	3900
	$7s^27p_{3/2}\,{}^2P_{3/2}$	8348	8273	7900
EA	$7s^27p^2\,{}^3P_0$	2483	2477	
	$7s^27p6d\,{}^1D_2$	1237	1314	
	$7s^27p^2\,{}^3P_1$	258	284	

[a] This value is obtained after applying an empirical correction, derived by analogy to other atoms. The MCDF calculated value is ~3600 cm^{-1}.

The orbital reversal occurs also for Lr^-, for which we predict a $7p_{1/2}^2\ {}^3P_0$ ground state, bound by some 2500 cm^{-1}. The next state of the anion is $7p6d$, bound by 1300 cm^{-1}. There may be a third bound state of the anion, $7p^2\ {}^3P_1$, but its calculated binding energy is too small to be sure of its existence.

D. Sources of error

Errors of a few hundred wave numbers, or up to 3%, occur in the calculated ionization potentials and excitation energies. More accurate results were naturally obtained for alkali-metal atoms (agreement within 20–30 cm^{-1} for Fr [17]), since the transitions there involve essentially single-electron states. Three approximations are used in the calculations and may be responsible for the errors. The first is the truncation of the Dirac-Coulomb-Breit Hamiltonian (1)–(5) after the α^2 terms. This truncation may not be valid for highly ionized heavy atoms, but Lindgren [34] has shown that it is quite accurate for neutral and weakly ionized species. This is corroborated by the small effect of the Breit term, which (being of order α^2) is included in the present work. The two other sources of error are the finite basis set and the truncation of the CC expansion (10) at the CCSD level. Both may contribute significantly and it is hard to apportion blame between the two without further studies.

V. SUMMARY AND CONCLUSION

A large number of transition energies were calculated for Yb, Lu, and Lr, including ionization potentials, excitation energies, and electron affinities of the atoms and some of their ions. Many electrons (30–40) were correlated, to account for core-valence polarization. High-l virtual orbitals were included (up to $l = 5$) to describe dynamic correlation. A comparison with experiment (when available) shows agreement within a few hundred wave numbers, with a few exceptions. Average errors are at least three times smaller than for previous calculations. We predict two bound states of Lu$^-$, $6p5d$ $^1D_2$ and $6p^2$ $^3P_0$, with binding energies of about 2100 and 750 cm^{-1}, respectively. The ground state of lawrencium is $^2P_{1/2}$, relativistically stabilized relative to $^2D_{3/2}$, the ground state of Lu. Two states of the Lr$^-$ anion are bound, $7p^2$ $^3P_0$ (by 2500 cm^{-1}) and $7p6d$ $^1D_2$ (by 1300 cm^{-1}). A third state ($7p^2$ $^3P_1$) may also be bound.

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[1] W. C. Martin, R. Zalubas, and L. Hagan, *Atomic Energy Levels — The Rare-Earth Elements*, U.S. Natl. Bur. Stand. Ref. Data Ser., U.S. Natl. Bur. Stand. Circ. No. NBS 60 (U.S. GPO, Washington, DC, 1978).

[2] For reviews of MCDF see I. P. Grant, Adv. Phys. **19**, 747 (1970); I. P. Grant and H. M. Quiney, Adv. At. Mol. Phys. **23**, 37 (1988).

[3] J.-P. Desclaux and B. Fricke, J. Phys. **41**, 943 (1980).

[4] V. A. Glebov, L. Kasztura, V. S. Nefedov, and B. L. Zhuikov, Radiochim. Acta **46**, 117 (1989).

[5] E. Johnson, B. Fricke, O. L. Keller, C. W. Nestor, Jr., and T. C. Tucker, J. Chem. Phys. **93**, 8041 (1990).

[6] I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Myers, and N. C. Pyper, Comput. Phys. Commun. **21**, 207 (1980); K. G. Dyall, I. P. Grant, C. T. Johnson, F. A. Parpia, and E. P. Plummer, *ibid.* **55**, 425 (1989).

[7] Z. Cai, V. Meiser Umar, and C. Froese Fischer, Phys. Rev. Lett. **68**, 297 (1992).

[8] E. Eliav, U. Kaldor, and Y. Ishikawa, Phys. Rev. Lett. **74**, 1079 (1995).

[9] I. Lindgren, in *Many-Body Methods in Quantum Chemistry*, edited by U. Kaldor, Lecture Notes in Chemistry Vol. 52 (Springer-Verlag, Heidelberg, 1989), p. 293; Nucl. Instrum. Methods Phys. Res. Sect. B **31**, 102 (1988).

[10] E. Lindroth, Phys. Rev. A **37**, 316 (1988); A.-M. Mårtensson-Pendrill, in *Numerical Determination of the Electronic Structure of Atoms, Diatomic and Polyatomic Molecules*, edited by M. Defranceschi and J. Delhalle (Kluwer, Dordrecht, 1989), p. 131; in *Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms*, edited by W. Johnson, P. Mohr, and J. Sucher, AIP Conf. Proc. No. 189 (AIP, New York, 1989), p. 305.

[11] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, Phys. Rev. A **39**, 3768 (1989); Z. W. Liu and H. P. Kelly, *ibid.* **43**, 3305 (1991); S. A. Blundell, W. R. Johnson, Z. Liu, and J. Sapirstein, *ibid.* **40**, 2233 (1989); S. A. Blundell, W. R. Johnson, and J. Sapirstein, Phys. Rev. Lett. **65**, 1411 (1990); Phys. Rev. A **43**, 3407 (1991).

[12] A.-M. Mårtensson-Pendrill, S. A. Alexander, L. Adamowicz, N. Oliphant, J. Olsen, P. Öster, H. M. Quiney, S. Salomonson, and D. Sundholm, Phys. Rev. A **43**, 3355 (1991); A. C. Hartly, E. Lindroth, and A.-M. Mårtensson-Pendrill, J. Phys. B **23**, 1990 (1990); A. C. Hartly and A.-M. Mårtensson-Pendrill, Z. Phys. D **15**, 309 (1990); J. Phys. B **24**, 1193 (1991); E. Lindroth and S. Salomonson, Phys. Rev. A **41**, 4659 (1990); E. Lindroth, H. Persson, S. Salomonson, and A.-M. Mårtensson-Pendrill, *ibid.* **45**, 1493 (1992).

[13] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem. **24**, 241 (1990).

[14] E. Ilyabaev and U. Kaldor, Chem. Phys. Lett. **194**, 95 (1992); Phys. Rev. A **47**, 137 (1993); J. Chem. Phys. **97**, 8455 (1992).

[15] E. Eliav, U. Kaldor, and Y. Ishikawa, Phys. Rev. A **49**, 1724 (1994).

[16] E. Eliav (Ilyabaev), U. Kaldor, and Y. Ishikawa, Chem. Phys. Lett. **222**, 82 (1994).

[17] E. Eliav, U. Kaldor, and Y. Ishikawa, Phys. Rev. A **50**, 1121 (1994).

[18] E. Eliav, U. Kaldor, and Y. Ishikawa, Int. J. Quantum Chem. Symp. **28**, 205 (1994).

[19] E. Eliav, U. Kaldor, and Y. Ishikawa, Phys. Rev. A **51**, 225 (1995).

[20] E. Eliav, U. Kaldor, P. Schwerdtfeger, B. A. Hess, and Y. Ishikawa, Phys. Rev. Lett. **73**, 3203 (1994).

[21] J. Migdalek and W. E. Baylis, Phys. Rev. A **33**, 1417 (1986).

[22] K. Koc and J. Migdalek, J. Phys. B **25**, 907 (1992).

[23] S. A. Kotochigova and I. I. Tuzipin, J. Phys. B **20**, 4759 (1987).

[24] J. Migdalek and W. E. Baylis, J. Quant. Spectrosc. Radiat. Transfer **37**, 521 (1987).

[25] S. H. Vosko, J. A. Chevary, and I. L. Mayer, J. Phys. B **24**, L225 (1991).

[26] S. H. Vosko and J. A. Chevary, J. Phys. B **26**, 873 (1993).

[27] J. Sucher, Phys. Rev. A **22**, 348 (1980); Phys. Scr. **36**, 271 (1987).

[28] Y. Ishikawa and H. M. Quiney, Phys. Rev. A **47**, 1732 (1993); Y. Ishikawa, *ibid.* **42**, 1142 (1990); Y. Ishikawa, R. Barrety, and R. C. Binning, Chem. Phys. Lett. **121**, 130 (1985).

[29] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed. (Springer-Verlag, Berlin, 1986).

[30] W. Kutzelnigg, Int. J. Quantum Chem. **25**, 107 (1984).

[31] R. E. Stanton and S. Havriliak, J. Chem. Phys. **81**, 1910 (1984).

[32] S. Huzinaga and M. Klobukowski, Chem. Phys. Lett. **212**, 260 (1993).

[33] G. L. Malli, A. B. F. Da Silva, and Y. Ishikawa, Phys. Rev. A **47**, 143 (1993).

[34] I. Lindgren, Nucl. Instrum. Methods Phys. Res. Sect. B **31**, 102 (1988); Phys. Scr. **T34**, 36 (1991).