

Relativistic coupled-cluster calculations for open-shell atoms

Ephraim Ilyabaev and Uzi Kaldor

School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

(Received 8 June 1992)

Ground- and excited-state energies are calculated by the relativistic coupled-cluster open-shell Fock-space method for Li, C, O, F, and Na and their ions. The coupled-cluster approximation including single and double excitations in a self-consistent manner, is implemented. The no-pair Dirac-Coulomb Hamiltonian is taken as the starting point. Mean-length basis sets of balanced Gaussian spinors are used to span the atomic orbitals.

PACS number(s): 31.20.Tz, 31.30.Jv, 31.50.+w

I. INTRODUCTION

Relativistic quantum mechanics and field theory are essential in order to model a wide range of observable phenomena in atomic and molecular physics to the accuracy demanded by many current experiments [1]. Efficient and accurate theoretical and computational methods, incorporating relativistic effects together with a good treatment of electron correlation, are required for the purpose. The past few years have seen an intensive development of relativistic many-body techniques in quantum chemistry and, in particular, the method of fully relativistic (Dirac-equation-based) many-body perturbation theory (RMBPT) [2,3]. The RMBPT provides a powerful and systematic method for calculating the properties of many-electron systems. The first few terms of the perturbation series suffice for accurate calculations of the properties of highly charged ions [4], but the method is less suitable for neutral atoms, where higher orders of RMBPT are non-negligible. The expressions for the higher orders become so complicated that direct perturbative studies are rarely carried out beyond second order. An alternative treatment is provided by so-called all-order methods, where infinite subclasses of contributions are summed. One of the most promising of these is the coupled-cluster (CC) formalism [5]. It leads to all-order equations, which upon iteration yield the order-by-order expressions for the Rayleigh-Schrödinger linked-diagram expansion. The formalism thus shares with the order-by-order approach the property of size extensivity, important for accurate calculations on heavy elements, where the relativistic effects are the most significant. The CC method gives electron correlation with high accuracy, and is widely applied in nonrelativistic atomic and molecular calculations [6]. The development of relativistic CC methods has been discussed [7], but few applications have appeared. The closed-shell relativistic CC scheme was used, both in numerical and finite-basis-set forms, for ground-state calculations of two- [8] and four- [9,10] electron atoms only, with the exception of our recent report [11] including the Ne and Ar atoms. Applications to open-shell systems are even fewer. To our knowledge, only the linearized coupled-cluster approach in the pair approximation, suitable for systems with just

one valence particle, was implemented for Li, Be⁺ [12], and Cs [13].

The starting point for our development of relativistic CC calculations in *c*-number theory is the time-honored relativistic “no-pair” Dirac-Coulomb Hamiltonian (H_{DC}), originally introduced by Sucher [14] to avoid the “continuum dissolution” problem associated with relativistic many-body calculations. We write this Hamiltonian as $H_{DC} = H_0 + V$, where (using atomic units)

$$H_0 = \sum_i \Lambda_i^+ [c\vec{\alpha}_i \cdot \vec{p}_i + c^2(\beta_i - 1) + V_{\text{nuc}}(i) + U(i)] \Lambda_i^+, \quad (1)$$

$$V = \sum_{i < j} \Lambda_i^+ \Lambda_j^+ \frac{1}{r_{ij}} \Lambda_j^+ \Lambda_i^+ - \sum_i \Lambda_i^+ U(i) \Lambda_i^+. \quad (2)$$

Here an arbitrary potential U was included in the unperturbed Hamiltonian H_0 and subtracted from the perturbation V . The potential U is chosen to approximate the effect of the electron-electron interaction; in particular, it may be the Dirac-Fock self-consistent-field (DFSCF) potential. The nuclear potential V_{nuc} includes the effect of finite nuclear size. The Λ^+ are projection operators onto the positive-energy states of the Dirac Hamiltonian in the potential $V_{\text{nuc}} + U$. Due to the presence of these operators, the Hamiltonian (1) has normalizable, bound-state solutions. Lindgren [7,15(a)] has shown that a well-defined subset of the full QED perturbation series may be based on this no-virtual-pair Hamiltonian. Omitted relativistic and QED effects can be identified, sorted in order of α (the fine-structure constant), and added later, if desired, either in a perturbative manner or in the usual coupled-cluster procedure. These effects include (1) in order $O(\alpha^2)$ —the leading, unretarded part of the transverse photon exchange (the Breit interaction)

$$B_{12} = -\frac{1}{2} [\vec{\alpha}_1 \cdot \vec{\alpha}_2 + (\vec{\alpha}_1 \cdot \vec{r}_{12})(\vec{\alpha}_2 \cdot \vec{r}_{12}/r_{12}^2)] / r_{12}; \quad (3)$$

(2) in order $O(\alpha^3)$ —retardation, negative-energy state effects, and radiative corrections.

The Coulomb potential $1/r_{12}$ describes the instantaneous electrostatic interaction, and the Breit potential (3) is the magnetostatic term. Adding the two leads to the best description of Lorentz invariance in relativistic interactions, and increases the accuracy of calculated fine-

structure splittings and inner electron bonding energies [3,16,17]. The potential (3) has been used in relativistic calculations for atoms, in particular in the DFSCF procedure [18–20], where effects through order α^2 are included in the zero-order Hamiltonian. Other relativistic atomic calculations [21–25], both Dirac-Fock and correlated, show that the Coulomb interaction alone yields good results for light elements ($Z < 20$). The latter approximation is used in the present work.

II. COMPUTATIONAL METHOD

In q -number theory, the Dirac-Coulomb Hamiltonian H_{DC} is rewritten in terms of normal ordered products of the spinor operators $\{r^+s\}$ and $\{r^+s^+ut\}$ [14,25],

$$H_N = H_{DC} - \langle 0 | H_{DC} | 0 \rangle \\ = \sum_{r,s} f_{rs} \{r^+s\} + \frac{1}{4} \sum_{r,s,t,u} \langle rs || tu \rangle \{r^+s^+ut\}, \quad (4)$$

where

$$\langle rs || tu \rangle = \langle rs | tu \rangle - \langle rs | ut \rangle \quad (5)$$

and

$$\langle rs | tu \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \Psi_r^*(\mathbf{x}_1) \Psi_s^*(\mathbf{x}_2) r_{12}^{-1} \Psi_t(\mathbf{x}_1) \Psi_u(\mathbf{x}_2). \quad (6)$$

Here f_{rs} and $\langle rs || tu \rangle$ are, respectively, one-electron DF and antisymmetrized two-electron Coulomb interaction matrices over Dirac four-component spinors. The effect of the projection operators Λ^+ is now taken over by the normal ordering, 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.

By adopting the no-pair approximation, a natural and straightforward extension of the nonrelativistic open-shell CC theory emerges. The multireference state-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 [15(b)], the effective Hamiltonian has the form

$$H_{\text{eff}} = PH\Omega P, \quad (7)$$

where Ω is the normal ordered wave operator,

$$\Omega = \{ \exp(S) \}. \quad (8)$$

In addition to the traditional decomposition into the sum of terms with different *total* (l) number of excited electrons, the excitation operator S may be partitioned according to the number of *valence holes* (m) and *valence particles* (n) to be excited,

$$S = \sum_{m \geq 0} \sum_{n \geq 0} \left\{ \sum_{l \geq m+n} S_l^{(m,n)} \right\}. \quad (9)$$

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 [26]. The equation for the (m, n) sector involves 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 $S^{(0,0)}$ 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. Presently our relativistic CC program includes the (0,0), (1,0), (2,0), (0,1), (0,2), and (1,1) sectors.

The lower index l in (9) goes, in principle, to the total number of electrons. In practice, it has to be truncated. The level of truncation reflects the quality of the approximation, i.e., the extent to which the effect of the complementary Q space is taken into account in the calculation of the effective Hamiltonian. The most common truncation level is at $l=2$. The resulting CCSD (coupled clusters with single and double excitations) 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. As negative-energy states are excluded from the Q space, the diagrammatic summations in the CC equations are carried out only within the subspace of the positive-energy branch of the DF spectrum.

The selection of the model space plays a crucial role in this method. From the practice of nonrelativistic calculations, it is known that intruder states [27], which spoil the convergence of the calculation, occur sometimes. The relativistic case may be expected to present even more difficulties because of fine-structure splittings. Careful construction of the model space may alleviate the problem. In particular, the so-called incomplete model space [28] may be useful in many cases. Our relativistic CC programs can implement complete as well as incomplete model spaces.

TABLE I. CCSD energies for Li and Na (a.u.). See scheme (10).

		Relativistic	Nonrelativistic
Li ⁺	1s ² 1S ₀	-7.276 447 2	-7.275 472 1
Li	2s ² 2S _{1/2}	-7.474 055 8	-7.473 241 6
	2p ² 2P _{1/2}	-7.406 205 5	-7.404 910 8
	2p ² 2P _{3/2}	-7.406 202 6	
	3s ² 2S _{1/2}	-7.350 107 7	-7.349 374 6
	3p ² 2P _{1/2,3/2}	-7.333 186 5	-7.332 327 8
Li ⁻	2s ² 1S ₀	-7.496 804 4	-7.495 972 2
Na ⁺	2p ⁶ 1S ₀	-162.074 431	-161.855 681
Na	3s ² 2S _{1/2}	-162.260 395	-162.041 389
	3p ² 2P _{1/2}	-162.184 524	-161.965 719
	3p ² 2P _{3/2}	-162.184 445	
Na ⁻	3s ² 1S ₀	-162.280 023	-162.061 024

TABLE II. Transition energies in Li and Na (cm^{-1}). Here and in subsequent tables, IP is the ionization potential, EA denotes electron affinity, and EE is the excitation energy, relative to the ground state of the same species. The sign $>$ is followed by the fine-structure splitting.

		Relativistic	Nonrelativistic	Expt. ^a
Li				
IP	$2s^2S_{1/2}$	43 370	43 346	43 487
EE	$2p^2P_{1/2}$	14 891.38	>0.63 14 997	14 903.66
	$2p^2P_{3/2}$	14 892.01		14 904.00
	$3s^2S_{1/2}$	27 204	27 186	27 206
	$3p^2P_{1/2,3/2}$	30 917	30 927	30 925
Li ⁻				
EA	$2s^2^1S_0$	4 993	4 989	5 000
Na				
IP	$3s^2S_{1/2}$	40 815	40 758	41 449
EE	$3p^2P_{1/2}$	16 651.44	>17.35 16 608	16 956.18
	$3p^2P_{3/2}$	16 668.79		16 973.38
Na ⁻				
EA	$3s^2^1S_0$	4 308	4 310	4 403

^aReference [37].

III. CALCULATIONS

Calculations were carried out for the Li, C, O, F, and Na atoms and their ions. The sequence of the open-shell CC calculations for the different systems is

$$M^+(0,0) \rightarrow M(0,1) \rightarrow M^-(0,2) \text{ for } M = \text{Li, Na}, \quad (10)$$

$$M^{+2}(0,0) \rightarrow M^+(0,1) \rightarrow M(0,2) \text{ for } M = \text{C}, \quad (11)$$

$$M^{-2}(0,0) \rightarrow M^-(1,0) \rightarrow M(2,0) \text{ for } M = \text{O}, \quad (12)$$

$$M^-(0,0) \rightarrow M(1,0) \rightarrow M^+(2,0) \text{ for } M = \text{F}. \quad (13)$$

In all cases, the Dirac-Fock equation was first solved in a basis of Gaussian-type functions (GTF) for the appropriate reference state in the (0,0) sector. Consecutive sets of CC equations were then iterated to convergence in the sequences indicated in (10)–(13). The Gaussian spinors were carefully chosen to avoid “variational collapse” [29] in the DF procedure. To this purpose, basis spinors were made to satisfy the condition of kinetic balance [30] and relativistic boundary conditions associated with a finite

nucleus, described here as a sphere of uniform proton charge [31]. The atomic masses used for Li, C, O, F, and Na were 6.939, 12.011 15, 15.994, 18.9984, and 22.9898, respectively. The speed of light c was taken to be 137.037 a. u.

The well-tempered (11s6p) GTF basis set of Matsouka and Huzinaga [32] was selected for the Li atom because of its compactness and special optimization for DF calculations. It was augmented by two sets of diffuse s and p functions with exponents 0.029 49 and 0.008 12, and two sets of polarization d functions with exponents 0.382 46 and 0.107 12. The uncontracted (13s8p2d) basis of Van Duijnveltdt [33] was used for C, O, and F, and for Na the (12s9p) uncontracted basis of McLean and Chandler [34] was augmented by two sets of diffuse s functions (exponents obtained by geometric extrapolation) and a d polarization function (exponent 0.4). Atomic functions with the same l but different k quantum number (e.g., $p_{1/2}$ and $p_{3/2}$) were expanded in terms of the same set of basis functions.

The DF equations were solved using the REATOM pro-

TABLE III. Fine structure of the $2p$ levels in Li (a.u.). Energies relative to Li^+ .

	$2p_{1/2}$	$2p_{3/2}$	$2p_{3/2} - 2p_{1/2}$
DF	-0.128 415 98 ^a -0.128 638 49 ^b	-0.128 413 46 ^a -0.128 635 94 ^b	0.000 002 52 ^a 0.000 002 55 ^b
CCSD	-0.129 758 34 ^a -0.130 242 80 ^b	-0.129 755 45 ^a -0.130 239 73 ^b	0.000 002 89 ^a 0.000 003 07 ^b
CCSD + Breit (PT)	-0.130 240 65 ^b	-0.130 239 07 ^b	0.000 001 56 ^b
Experiment			0.000 001 53 ^c

^aPresent work.

^bReference [12].

^cReference [37].

TABLE IV. CCSD energies of C, O, and F (a.u.). See schemes (11)–(13).

		Relativistic	Nonrelativistic
C ⁺	2s ² 1S ₀	−36.543 785 9	−36.527 194 7
C ⁺	2p ² P _{1/2}	−37.435 168 5	−37.418 478 2
	2p ² P _{3/2}	−37.434 833 3	
C	2p ² P ₀	−37.842 405 0	−37.825 905 6
	2p ² P ₁	−37.842 323 7	
	2p ² P ₂	−37.842 162 4	
O ^{−2}	2p ⁶ 1S ₀	−74.732 350 5	−74.676 750 0
O [−]	2p ⁵ 2P _{1/2}	−75.054 198 4	−74.998 116 9
	2p ⁵ 2P _{3/2}	−75.053 230 8	
O	2p ⁴ 2P ₀	−74.999 714 1	−74.943 349 9
	2p ⁴ 2P ₁	−74.998 859 8	
	2p ⁴ 2P ₂	−74.998 443 0	
F [−]	2p ⁶ 1S ₀	−99.855 110 3	−99.763 154 3
F	2p ⁵ 2P _{1/2}	−99.748 026 2	−99.655 008 9
	2p ⁵ 2P _{3/2}	−99.745 972 5	
F ⁺	2p ⁴ 3P ₀	−99.102 154 6	−99.008 583 8
	2p ⁴ 3P ₁	−99.100 507 5	
	2p ⁴ 3P ₂	−99.099 712 0	

gram from the MOTECC scientific package [35]. Special codes were written for the calculation of integrals that do not appear in DF calculations (and are therefore not included in MOTECC), and for performing integral transformations from basis spinors to atomic ones. Our nonrelativistic coupled-cluster programs [36] were modified to allow for the use of Dirac four-vectors. As a test of this program, it was used in nonrelativistic *spin-orbital* correlation calculations of open-shell atomic systems, giving full agreement with corresponding *orbital* nonrelativistic CC calculations.

IV. RESULTS AND DISCUSSION

The results of relativistic and nonrelativistic coupled-cluster calculations for the atomic systems studied are shown and compared with experiment [37,38] in Tables I–V. Tables I and II show the results for alkali-metal atoms Li and Na and their ions. The accuracy of the total relativistic energies is comparable to that of the nonrelativistic energies computed in the same Hilbert space (Table I). Transition energies (Table II) are close to experimental values. The considerable relative error in the fine-structure splitting of the 2p²P states of Li is probably due to neglecting the Breit interaction, which strongly affects this splitting [12,17]. Evidence to that is presented

TABLE V. Transition energies of C, O, and F (cm^{−1}).

		Relativistic	Nonrelativistic	Expt. ^a
C ⁺	IP	2p ² P _{1/2}	195 637	196 659
	EE	2p ² P _{3/2}	74	64
C	IP	2p ² 3P ₀	89 379	90 878.3
	EE	2p ² 3P ₁	18	16.4
	EE	2p ² 3P ₂	53	43.5
O	EA	2p ⁴ 3P ₀	11 958	11 818.7
	EE	2p ⁴ 3P ₁	188	158.5
	EE	2p ⁴ 3P ₂	279	226.5
F	EA	2p ⁵ 2P _{1/2}	23 502	27 555
	EE	2p ⁵ 2P _{3/2}	451	404
F ⁺	IP	2p ⁴ 3P ₀	141 753	140 554
	EE	2p ⁴ 3P ₁	362	342
	EE	2p ⁴ 3P ₂	536	491

^aReferences [37,38].

in Table III, which shows that our values are similar to those of Blundell *et al.* [12] without the Breit term, and it is the latter that brings their results close to experiment. CCSD correlated energies and transition energies of the C, O, and F atoms are collected in Tables IV and V. As expected, relativistic effects increase rapidly with the atomic number, from 1 mhartree for lithium to 0.2 hartree for sodium. This is the first presentation of relativistic open-shell coupled-cluster results for atoms with more than one valence electron. The results should not be regarded as definitive, since the basis sets used are too small (especially in high- l channels) to approach convergence for these systems [3,25]. Still, agreement with experimental transition energies and (more important for relativistic calculations) fine-structure splittings is quite good. Our computational procedures and programs are now being improved, so that bigger and better bases may be used in the future.

V. SUMMARY AND CONCLUSION

A relativistic open-shell coupled-cluster scheme applicable to many-electron atomic and molecular systems has

been presented. Test calculations of the ground and low-lying excited states on some first- and second-row atoms and ions were performed. The relativistic CC program is limited at present to its CCSD form. The Breit interaction has been neglected, and the two-electron interaction is treated "nonrelativistically" as the instantaneous Coulomb repulsion. Work is now in progress on the inclusion of the Breit interaction in the scheme. Extensions to higher orders of the excitations and to further sectors of the Fock space are also planned.

ACKNOWLEDGMENTS

The research reported here was supported by the U.S.-Israel Binational Science Foundation and by the Basic Research Foundation administered by the Israeli Academy of Sciences and Humanities. E. I. thanks the Ministry of Absorption for support.

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