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Open-shell relativistic coupled-cluster method with Dirac-Fock-Breit wave functions: Energies of the gold atom and its cation

Ephraim Eliav* and Uzi Kaldor
School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

Yasuyuki Ishikawa
Department of Chemistry, University of Puerto Rico, P.O. Box 23346, San Juan, Puerto Rico 00931-3346

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The relativistic Fock-space coupled-cluster method for the direct calculation of ionization potentials and excitation energies (including fine structure) is presented and applied to atomic Au and its ions. The no-pair Dirac-Coulomb-Breit Hamiltonian is taken as the starting point. The CCSD approximation is implemented (where CCSD indicates coupled cluster with single and double excitations), which includes single and double virtual excitations in a self-consistent manner, incorporating therefore the effects of the Coulomb and Breit interactions to all orders in these excitations. A rather large basis set ($21s\,17p\,11d\,7f$) of kinetically balanced Gaussian spinors is used to span the atomic orbitals. All calculated energies (ionization potential and electron affinity of Au, excitation energies of Au and Au$^+$) agree with experiment to 0.1 eV or better, with an average error of 0.06 eV. Fine structure splittings are accurate to better than 0.01 eV.

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I. INTRODUCTION

The relativistic contraction and stabilization of the *ns* valence shell (n = 4–6) undergoes a local maximum at the coinage metals, group 11 [1]. This is known in the literature as the "gold maximum," as the gold atom shows pronounced relativistic effects on its physical and chemical properties. Nonrelativistic calculations on the gold atom and its compounds lead to qualitatively incorrect results, e.g., reverse order of the first two excited states, ^2D and ^2P [2]. The inclusion of the leading relativistic terms in the Hamiltonian improves the situation dramatically (see [3] for a recent discussion). The gold atom and its compounds have recently become the subject of intense investigations [1,3], both because of their inherent interest and as testing grounds for relativistic quantum mechanical methods. While many of the relativistic effects on atomic and molecular structure may be estimated by perturbation theory or model (pseudopotential) techniques, it is desirable to have a first-principles method which incoporates relativity and correlation to high order, both for accurate prediction of atomic and molecular properties and as a check on more approximate models. An important issue is the nonadditivity of relativity and correlation effects in high-Z atoms, which may be investigated by a scheme including both effects *ab initio*.

The relativistic many-body Hamiltonian cannot be expressed in closed potential form. The nonrelativistic many-body approach may be extended to the relativistic domain by applying a formalism based on effective potentials, obtained with arbitrary accuracy from quantum electrodynamics (QED), as suggested by Lindgren [4]. Two major modifications are required upon going from the nonrelativistic to the relativistic formulation: (i) the Pauli-Schrödinger spin orbitals are replaced by four-component Dirac spinors, which may have positive as well as negative energies, and (ii) the instantaneous particle-particle Coulomb interactions are supplanted by the irreducible multiphoton effective potentials, together with radiative corrections and renormalization counterterms.

The many-body formalism used in nonrelativistic quantum mechanics for correlation effects may be employed in the relativistic case, with proper changes taking into account the modification of orbital form and potential terms. Different levels of approximation are possible, depending on the order of relativistic and QED effects included. The first rigorous level beyond the nonrelativistic scheme is based on modification (i) and on the potential derived from the single-photon-exchange S-matrix with no consideration of negative energy states and radiative corrections. The Hamiltonian formed this way is called the projected Dirac-Coulomb-(Breit or Gaunt) Hamiltonian. Its use was advocated by Sucher [5], to avoid the "continuum dissolution" problem associated with negative energies in relativistic many-body calculations. We write this Hamiltonian as

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

where (in atomic units)

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

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

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

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*Formerly Ilyabaev.

Here h_D is the one-electron Dirac Hamiltonian. An arbitrary potential U was 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 $V_{\rm nuc}$ includes the effect of finite nuclear size. The 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 (NVPA), since virtual electron-positron pairs are not allowed in intermediate states. The form of the effective potential $V_{\rm eff}$ depends on the gauge used. Here we shall consider the two most popular gauges, the Feynman gauge and the Coulomb gauge, in which cases the effective interaction becomes in atomic units [4],

$$V_{\rm eff}^F(\omega) = (1 - \boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2)\frac{e^{i\omega r_{12}}}{r_{12}} , \tag{5}$$

$$V_{\rm eff}^C(\omega) = \frac{1}{r_{12}} - \boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 \frac{e^{i\omega r_{12}}}{r_{12}} + (\boldsymbol{\alpha}_1 \cdot \boldsymbol{\nabla})(\boldsymbol{\alpha}_2 \cdot \boldsymbol{\nabla})\frac{e^{i\omega r_{12}} - 1}{\omega^2 r_{12}} , \tag{6}$$

respectively. The ω parameter is related to the energy transfer between the virtual photon and the electrons and is included only in exponential terms, which physically mean retardation of the interaction. When only the positive part of the energy spectrum is present, the energy parameter ω is first order in α, the fine-structure constant. Terms involving the Dirac operators $\boldsymbol{\alpha}$ and β that mix the large and small components of the wave function are of the same order. The one-photon potential, correct to order α^2, is then

$$V_{\rm eff}^F(\omega) = \frac{1}{r_{12}} + G_{12} - \frac{1}{2}\omega^2 r_{12} + O(\alpha^3) , \tag{7}$$

$$V_{\rm eff}^C(\omega) = \frac{1}{r_{12}} + B_{12} + O(\alpha^3) , \tag{8}$$

where

$$G_{12} = -\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 / r_{12} \tag{9}$$

and

$$B_{12} = -\tfrac{1}{2}\left[\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + (\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})/r_{12}^2\right]/r_{12} \tag{10}$$

are the well-known frequency-independent (unretarded) Gaunt and Breit interactions respectively. The Coulomb potential $1/r_{12}$ describes the instantaneous electrostatic interaction, and the Gaunt or Breit potentials are the magnetostatic terms. Adding the latter 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 [6–8]. Equation (6) shows that only the magnetic part is retarded in Coulomb gauge, while the Coulomb interaction is instantaneous. Hence, the unretarded interaction in that gauge, the Coulomb-Breit potential, is correct to order α^2 [see Eq. (8)]. In the Feynman gauge (5) the Coulomb interaction is also retarded, and the leading part of the retardation must be considered to achieve the same accuracy [Eq. (7)].

The no-pair approach with unretarded Coulomb-Breit interparticle potential accounts for relativity up to order α^2. High-order QED effects, such as Lamb shifts and effects of negative energy states, appear first in order α^3 and are omitted. This scheme is now widely used and is expected to be quite accurate for most neutral and weakly ionized atoms of the naturally occurring elements. The no-pair method forms the basis for modern versions of relativistic many-body perturbation theory (MBPT), which is a powerful and systematic method for calculating electron correlation effects in many-electron systems (for recent reviews see [6]). The first few terms of the perturbation series suffice for highly charged ions [9], but the method is less suitable for neutral atoms, where higher orders of MBPT are non-negligible. The expressions for the higher orders become complicated, and direct perturbative studies are rarely carried out beyond the second-order correction to the wave function or the third-order energy correction. 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 [10,11]. 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, for which relativistic effects are most significant. The CC method gives electron correlation with high accuracy, and is widely applied in nonrelativistic atomic and molecular calculations [12].

The development and implementation of reliable relativistic CC schemes is a challenging problem in the study of many-electron systems. Several groups are working in this direction, but only few applications have appeared. A numerical procedure for solving relativistic differential many-body equations with Coulomb potential based on the pair approximation of the CC approach has been developed by Lindgren and co-workers [10,11] and implemented to two-electron atomic systems [13]. A specific problem arising in this work is the application of the projection operators, which is nontrivial with the differential-equations technique.

A different approach to the many-body problem involves the use of discrete basis sets of local or global functions. The implementation of the projection operators is easier in the frame of this scheme than in the differential-equations method. Applying the projection operators is reduced simply to summation over the positive energy part of the one-electron spectrum. Relativistic CC techniques based on local splines (piecewise polynomial fitting) were developed by Blundell *et al.* and applied to closed-shell two- and four-electron atoms [14]; in linearized form the method was applied to the one-valence-electron open-shell Li, Be$^+$ [15] and Cs [16]. A different type of local basis set was introduced by Salomonson and Öster [17], who discretized the radial space. This technique is similar in spirit to the spline method and can be regarded as a limiting case of that method (single-point representation rather than polynomial fitting). The method has been applied to energy calculations of atomic Be [18] and to evaluating hyperfine structure, transition energies, and parity-nonconservation effects in some one-valence-electron systems [19]. All relativistic CC implementations discussed above neglect the Breit interaction and treat the two-electron interaction "nonrelativistically" as the instantaneous Coulomb repulsion. Lindroth and Salomonson [20] have recently extended the method of Salomonson and Öster to include the Breit interaction [Eq. (10)] self-consistently in the Dirac-Fock-Breit orbitals and then in the pair-correlation procedure, combined with Coulomb interactions to all orders. Thus the NVPA scheme correct to order α^2 was realized. This CC version has been applied to the ground-state energy of the Be atom [21] and to transitions in He-like Ar [20] and Be-like Fe and Mo [22].

Quantum chemical methods mostly use basis sets of global analytical functions such as Slater-type or Gaussian-type orbitals. A relativistic CC method in a discrete global analytical spinor basis has been developed and implemented recently by our group [23–25]. Using the Dirac-Coulomb Hamiltonian, we calculated the ground-state energies of the closed-shell Ne and Ar atoms [23]. An open-shell version of the method was applied to atomic ground and excited states with one or two electrons and/or holes relative to a closed-shell state [24,25]. This approach is similar in content to the methods based on local basis functions discussed above, since they use a discrete representation of the Dirac spectrum, with subsequent evaluation of many-body diagrams using finite summation. The principal advantage of the analytical expansion technique is the speed and accuracy with which the two-electron integrals over the basis functions may be evaluated. The transformation of these integrals into matrix elements of the Hamiltonian may be performed using linear algebra techniques, and the scheme may be programmed very effectively on modern computers [26]. Many of the high-performance computer codes developed in nonrelativistic quantum chemistry can be adapted without substantial modification to the relativistic case [27], and relativistic *ab initio* calculations of electronic correlation in molecules become feasible. Gaussian-type functions have certain advantages as bases for relativistic quantum chemistry, in addition to the well-known simplicity of calculating two-electron integrals [28]. Basis sets of Gaussian spinors (G spinors) show no near-linear-dependence difficulties reported with sets of S spinors (with Slater-type functions). G spinors mimic exactly the behavior of the wave function near the origin of a uniformly charged spherical nucleus. This is the main reason why G-spinor expansions exhibit fast and smooth convergence when the nucleus is modeled as a uniform proton charge ball [28,29]. The relativistic CC approach based on G-spinor basis sets generates a compact representation of the Dirac spectrum and allows investigation of many-electron systems based on existing quantum chemical packages [23–25].

The present calculations on the Au atom and its ions were done by extending our CC programs [23–25] to include the Breit interaction. The atomic integrals, Dirac-Fock-Coulomb (DFC), and Dirac-Fock-Breit (DFB) functions were calculated by programs written by Ishikawa and co-workers [28]. The computations were performed on the IBM RS6000 workstations at Tel Aviv University.

II. COMPUTATIONAL METHOD

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 $\{r^+s^+ut\}$ [5,28]

$$\begin{aligned} H &= H_+ - \langle 0|H_+|0\rangle \\ &= \sum_{rs} f_{rs}\{r^+s\} + \frac{1}{4}\sum_{rstu}\langle rs||tu\rangle\{r^+s^+ut\}, \end{aligned} \tag{11}$$

where

$$\langle rs||tu\rangle = \langle rs|tu\rangle - \langle rs|ut\rangle \tag{12}$$

and

$$\begin{aligned} \langle rs|tu\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \Psi_r^*(\mathbf{x}_1)\Psi_s^*(\mathbf{x}_2)(r_{12}^{-1} + B_{12}) \\ \times \Psi_t(\mathbf{x}_1)\Psi_u(\mathbf{x}_2). \end{aligned} \tag{13}$$

Here, 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 braces in the equations 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.

By adopting the no-pair approximation, a natural and straightforward extension of the nonrelativistic open-shell CC theory emerges. 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 [11], the effective Hamiltonian has the form

$$H_{\text{eff}} = PH\Omega P\ , \tag{14}$$

where Ω is the normal-ordered wave operator,

$$\Omega = \{\exp(S)\}. \tag{15}$$

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,

$$S = \sum_{m\geq 0}\sum_{n\geq 0}\left(\sum_{l\geq m+n} S_l^{(m,n)}\right) . \quad (16)$$

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 $S^{(0,0)}$ 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 (16) 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 cluster 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 $H_{\rm eff}$ diagrams may also be separated into core and valence parts,

$$H_{\rm eff} = H_{\rm eff}^{\rm core} + H_{\rm eff}^{\rm val}, \quad (17)$$

where the first term on the right-hand side consists of diagrams without any external (valence) lines and includes core-electron correlation. The eigenvalues of $H_{\rm eff}^{\rm val}$ will then give directly the transition energies from the reference state, with correlation effects included for both initial and final states. The physical significance of these energies depends on the nature of the model space. Thus, electron affinities may be calculated by constructing a model space with valence particles only [$(0,n)$ sectors, $n > 0$], ionization potentials are given using valence holes [$(n,0)$ sectors, $n > 0$], and both valence types are required to describe excitations out of the reference state [(m,n) sectors, $m,n > 0$]. The method has been applied with the Dirac-Coulomb Hamiltonian in the $(n,0)$ and $(0,n)$ sectors, with $n = 1, 2$ [24], and in the (1,1) sector [25].

Experience with nonrelativistic coupled-cluster calculations shows that the selection of the model space plays a crucial role. The commonly used complete model space comprises all possible distributions of the valence electrons (or holes) in the valence orbitals. Frequently, one has to resort to incomplete model spaces [30,31] to ensure convergence. We have included the possibility of using the incomplete-model-space formalism in our relativistic CC program codes.

III. CALCULATIONS

Calculations were carried out for the Au atom and its cation and anion. Two sequences of the open-shell CC calculations were used, starting from the two closed-shell systems Au$^+$ and Au$^-$ and going through valence-particle and valence-hole sectors, respectively:

$$\mathrm{Au}^+(0,0) \rightarrow \mathrm{Au}(0,1) \rightarrow \mathrm{Au}^-(0,2) , \quad (18)$$

$$\mathrm{Au}^-(0,0) \rightarrow \mathrm{Au}(1,0) \rightarrow \mathrm{Au}^+(2,0) . \quad (19)$$

The Dirac-Fock equation was first solved in a basis of Gaussian-type functions for the appropriate reference state in the (0,0) sector. Consecutive sets of CC equations were then iterated to convergence in the sequences indicated. The Gaussian spinors were carefully chosen to avoid "variational collapse" [32] in the DF procedure. To this purpose, basis spinors were made to satisfy the condition of kinetic balance [33] and relativistic boundary conditions associated with a finite nucleus, described here as a sphere of uniform proton charge [28]. The atomic mass of Au was taken as 196.967, and the speed of light as 137.037 atomic units.

The basis set of Pizlo *et al.* [3] in its uncontracted form was selected for our calculations. It consists of $21s\,17p\,11d\,7f$ functions. Atomic orbitals with the same l and different k values (e.g., $p_{1/2}$ and $p_{3/2}$) were expanded in the same set of basis functions. The relativistic CC programs used previously [23–25] were modified to take advantage of the angular decomposition of the relativistic CC equations in a central field. Using standard angular-momentum graphical techniques [11], the Gold-

TABLE I. Total energies of the closed-shell systems Au$^+$ and Au$^-$ (hartrees).

	Au$^+$		Au$^-$	
	Noncorrelated	Correlation[a]	Noncorrelated	Correlation[b]
HF	−17863.463009	−1.297561	−17863.683925	−1.370182
DFC	−19029.013225	−1.361496	−19029.320775	−1.464362
DFB	−19007.423851	−1.364300	−19007.730628	−1.466900

[a] External two shells ($4s$ to $5d$).

[b] External three shells ($4s$ to $6s$).

TABLE II. Transition energies in Au (eV). These are the results of correlated coupled-cluster calculations, starting from Dirac-Fock-Coulomb (DFC), Dirac-Fock-Breit (DFB), or nonrelativistic orbitals. IP is the ionization potential, EA denotes electron affinity, and EE the excitation energy relative to the ground state. FS denotes fine-structure splittings.

			DFC	DFB	Nonrel.^{a}	Expt.^{b}
IP	$5d^{10}6s$	$^2S_{1/2}$	9.101	9.086	6.981	9.22
			8.992^c	8.977^c	6.799^c	
EE	$5d^9 6s^2$	$^2D_{3/2}$	2.661^c	2.669^c	5.301^c	2.658
	$5d^9 6s^2$	$^2D_{5/2}$	1.115^c	1.150^c	5.301^c	1.136
	FS	^2D	−1.546^c	−1.519^c	0	−1.522
	$5d^{10}6p_{1/2}$	$^2P_{1/2}$	4.723	4.720	3.313	4.632
	$5d^{10}6p_{3/2}$	$^2P_{3/2}$	5.193	5.184	3.313	5.105
	FS	^2P	0.470	0.466	0	0.473
EA	$5d^{10}6s^2$	$^1S_0$	2.278^c	2.269^c	1.267^c	2.31
			2.241	2.232	1.236	

[a] Nonrelativistic limit calculated with $c = 10^5$ a.u.

[b] Reference [35].

[c] Energies calculated with scheme (19). All others use scheme (18).

stone diagrams were decomposed in terms of vector coupling coefficients, expressed by angular-momentum diagrams, matrix elements of the reduced Coulomb-Breit interaction, and excitation amplitudes S of (15). The reduced version of the equations for one- and two-electron excitations was then derived [34] with the help of the Jucys-Levinson-Vanagas theorem. This approach allows us to use large basis sets for high-accuracy results.

IV. RESULTS AND DISCUSSION

The total energies of the closed-shell Au$^+$ and Au$^-$ without and with relativistic and correlation effects are shown in Table I. The nonrelativistic limit was obtained by setting the speed of light c to 10^5 a.u. The $4s\,4p\,4d\,4f\,5s\,5p\,5d$ electrons were correlated, with the $6s$ added for the anion. The relativistic energy lowering (the difference between Hartree-Fock and Dirac-Fock energies) is very large, over 1100 hartrees. The Breit term increases the total energy by 21.6 hartrees. Most of these contributions come from the inner shells of the atom. Relativistic and correlation effects are nonadditive. Correlation of the two external shells of Au$^+$ is 64 millihartrees larger (in absolute value) in the relativistic than in the nonrelativistic approximation, with the difference going up to 94 millihartrees for Au$^-$. Inclusion of the Breit interaction increases correlation by 2–3 millihartrees. These effects are expected to be even larger for the inner shells.

The nonrelativistic and relativistic (with and without the Breit interaction) coupled-cluster ionization potential, electron affinity, and excitation energies of the Au atom are shown and compared with experiment [35] in Table II. Table III presents excitation energies of Au$^+$. The nonrelativistic approximation gives a very poor description of the energy spectrum of the atom and ion. The relativistic energies are in very good agreement with experiment. The largest error, 0.12 eV, is in the ionization potential of the atom. The average error of the ten reported energies for Au and Au$^+$ is 0.06 eV. These remaining errors are ascribed to deficiencies in the basis and to the truncation of the coupled-cluster expansion. The fine-structure splittings are also quite close to experiment (better than 0.01 eV), especially when the Breit interaction is included. It should be noted that the splittings are of the same order as many of the separations between different LS levels.

Table II includes results obtained by the two schemes described above [Eqs. (18),(19)], which start from the closed-shell systems Au$^+$ and Au$^-$ respectively. The difference between the two sets of values is not large, but significant (0.1 eV for the ionization potential of the atom, 0.03 eV for the electron affinity). As may be expected, Au$^+$ is a better starting point for the ionization potentials, whereas Au$^-$ is better for the electron affinity.

We have found no correlated four-component treatment of the atom to compare with the results reported above. Pizlo *et al.* [3] carried out one-component calculations of the Au ionization potential and electron affinity, as well as the *LS averages* of the excitation energies, without fine structure. Their results with the same basis are within 0.05 eV of ours. Schwerdtfeger's work [36] using pseudopotentials and including correlation by quadratic configuration interaction with single and double excitations and approximate triples QCISD(T) gave much larger errors, 0.3 eV for the ionization potential and 0.2 eV for the electron affinity.

TABLE III. Excitation energies of Au$^+$ (eV) calculated with scheme (19).

	DFC	DFB	Nonrel.^{a}	Expt.^{b}
$5d^9(^2D_{5/2})\,6s^2\ ^3D_3$	1.872	1.907	6.245	1.864
$5d^9(^2D_{5/2})\,6s^2\ ^3D_2$	2.207	2.240	6.245	2.187
$5d^9(^2D_{5/2})\,6s^2\ ^3D_1$	3.484	3.491	6.245	3.442
FS ($^3D_3 - {}^3D_2$)	0.335	0.333	0	0.323
FS ($^3D_2 - {}^3D_1$)	1.277	1.251	0	1.255
$5d^9(^2D_{3/2})\,6s^2\ ^1D_2$	3.724	3.734	6.707	3.672

[a] Nonrelativistic limit calculated with $c = 10^5$ a.u.

[b] Reference [35].

V. SUMMARY AND CONCLUSION

A relativistic open-shell coupled-cluster scheme applicable to direct calculation of ionization potentials and excitation energies of many-electron systems has been presented. Test calculations on the low-lying excited states of Au and Au^+ were performed, giving highly satisfactory results for excitation energies and fine-structure splittings. The relativistic CC program is limited at present to its CCSD form. The Coulomb-Breit potential was used, which is correct to order α^2. Work is now in progress on extensions to higher orders of the excitations and to further sectors of the Fock space. Molecular relativistic CC calculations are also planned.

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