Relativistic coupled cluster calculations of the energies for rubidium and cesium atoms

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Ionization potentials and excitation energies of rubidium and cesium atoms are computed using the relativistic coupled cluster (CC) method. The effect of electron correlations on the ground and excited state properties is investigated using different levels of CC approximations and truncation schemes. The present work demonstrates that the *even-parity channel* truncation scheme produces results almost as accurate as obtained from the *all-parity channel* approximation scheme at a reduced computational cost. The present study also indicates that for a given basis the linearized CC method tends to overestimate the ground and excited state properties compared to the full CC method. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1621616]

I. INTRODUCTION

The ground and excited state properties of alkali metal atoms are subject of theoretical and experimental interest because of their simple electronic structure, having one valence electron well separated from the inner core. Moreover, the heavier alkali metal atoms, such as rubidium, cesium, and francium, etc. are prime candidates to probe for physics that departs from the predictions of the Standard Model of elementary particle physics. In recent years, high-precision experiments, measuring the parity-nonconserving $6s \rightarrow 7s$ transition of Cs,[1] have shown that atomic experiments are competitive in investigating weak interactions between elementary particles. High precision atomic calculations are, therefore, necessary to obtain information about the weak interaction constant.[2]

Extensive theoretical studies on the ground and excited state properties of systems containing heavy atoms have shown that accurate prediction of transition energies and related properties requires the incorporation of both relativistic and high order correlation and relaxation effects as these effects are strongly entangled. The relativistic and dynamical electron correlation effects can be incorporated in many-electron systems through a variety of many-body methods of which the coupled cluster method (CCM) has emerged as one of the most powerful and effective tool for a high precision description of electron correlations in many-electron systems. The CCM is an all-order nonperturbative scheme, and therefore, the higher order electron correlation effects can be incorporated more efficiently than using the order-by-order diagrammatic many-body perturbation theory (MBPT). The CC method is size-extensive, a property which has been

found to be crucial for an accurate determination of state energies, bond cleavage energies and related spectroscopic constants. Since the order-by-order MBPT expansion terms are directly related to the CC equations (as the latter is an all-order version of the former scheme), the CC results can be improved by adding the important omitted diagrams with the aid of low order MBPT.

The ground and excited states of Rb and Cs atoms were previously studied by Johnson *et al.*[3] and Blundell *et al.*[4] using diagrammatic many-body perturbation theory (MBPT). Since the expressions beyond second order MBPT are complicated, these direct perturbative studies were limited to third and partial fourth order. Later Blundell *et al.*[5] and Safronova *et al.*[6] incorporated all order effects through a linearized CC scheme (with partial triples) and computed the ground and excited state properties of the alkali metal atoms. Similar but more rigorous theoretical studies on the ground and excited states of alkali-metal atoms were reported by Eliav *et al.*[7] who employed a full CCSD to compute the ionization and excitation energies of alkali metal atoms. However, in their full CCSD calculations, partial triples and deep core excitations were not included. It is, therefore, desirable to incorporate these two factors in the CC-scheme to explore and identify their effects on the ground and excited state properties.

In this article, we compute the ground and excited state properties of Rb and Cs using the LCCSD and CCSD scheme (with and without partial triples) to estimate the non-linear effects arising from CCSD and to access the relative performance and accuracy of these two schemes. Here, we study the effect of dynamical electron correlations arising from doubly excited cluster amplitudes whose first order contribution to the electron correlation is zero due to a Coulomb selection rule. This work also investigates the correla-

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tion contribution of the deep-lying core orbitals to the ground and excited state properties.

Section II briefly reviews the open-shell CC method and the inclusion of partial triples excitations. Computational details and results are discussed in the subsequent section.

II. METHODOLOGY: OPEN-SHELL CC THEORY FOR ENERGY-DIFFERENCES

The Dirac–Coulomb Hamiltonian for a many-electron system can be conveniently written as

$$H = \sum_{i=1}^{N} [c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)mc^2 + V_{\text{nuc}}(r_i)]$$

$$+ \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{2.1}$$

in which the Dirac operators $\boldsymbol{\alpha}$ and β are expressed by the matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \tag{2.2}$$

where $\boldsymbol{\sigma}$ stands for the Pauli matrices and I is the 2×2 unit matrix. To capture the effect arising from finite-size-nuclear correction, we have used a charge distribution inside the Fermi nucleus of the form,

$$\rho_{\text{Fermi}}^{\text{nuc}} = \rho_0 [1 + \exp((r-c)/a)]^{-1},$$

where c is the cut-off radius at which $\rho_{\text{Fermi}}^{\text{nuc}} = \rho_0/2$. The parameter a is related to skin thickness (t) by

$$t = 4 \ln 3 a.$$

In the present calculation skin thickness (t) is set to 2.30 fm.

In the CC approach, we begin with the N-electron closed-shell Dirac–Fock (DF) reference state $|\Phi\rangle$ and write the exact ground state as

$$|\Psi\rangle = e^T |\Phi\rangle, \tag{2.3}$$

where T is the hole-particle electron excitation operator. The Schrödinger equation

$$He^T|\Phi\rangle = Ee^T|\Phi\rangle \tag{2.4}$$

leads to the exact ground state energy E. However, it is technically simpler to define first the normal ordered Hamiltonian,

$$\tilde{H} \equiv H - \langle\Phi|H|\Phi\rangle = H - E_{\text{DF}}, \tag{2.5}$$

with the DF energy E_{DF} and then solve the modified Schrödinger equation,

$$\tilde{H}e^T|\Phi\rangle = (E - E_{\text{DF}})e^T|\Phi\rangle \equiv E_{\text{corr}}e^T|\Phi\rangle. \tag{2.6}$$

Premultiplying by e^{-T} and projecting on $\langle\Phi|$ we obtain the ground state correlation energy,

$$\langle\Phi|\bar{H}|\Phi\rangle = E_{\text{corr}}, \tag{2.7}$$

where we have defined the dressed, normal ordered Hamiltonian

$$\bar{H} = e^{-T}\tilde{H}e^T = H + [H,T] + \tfrac{1}{2}[[H,T],T] + \cdots. \tag{2.8}$$

The cluster amplitude (T) determining equations are obtained by projecting Eq. (2.6) onto the N-electron excited determinants $\langle\Phi^*|$,

$$\langle\Phi^*|\bar{H}|\Phi\rangle = 0. \tag{2.9}$$

Equations (2.7) and (2.9) are the closed-shell coupled cluster equations. In the first step, the set of equations (2.9) are solved to obtain the cluster amplitudes T, which are used to construct the dressed Hamiltonian $\bar{H}$ to evaluate the correlation energy E_{corr}. In the CCSD approximation, the cluster operator T is composed of one- and two-body excitation operators, i.e., $T = T_1 + T_2$, which are expressed in terms of second quantization. Equation (2.9) can be expressed in the following matrix form:

$$A + B \otimes T = 0 \quad \text{(LCCSD)}, \tag{2.10}$$

and

$$A + B(T) \otimes T = 0 \quad \text{(CCSD)}, \tag{2.11}$$

where A is a constant vector which consists of the elements $\langle\Phi^*|\tilde{H}|\Phi\rangle$ and T is the vector of the excitation amplitudes. Since the matrix $B(T)$ itself depends on the cluster amplitudes, Eq. (2.11) is solved iteratively. At this juncture, we emphasize that due to the spherical symmetry of atoms, the above derived equations can be separated into a radial and an angular part, which considerably simplifies the computational effort. The radial Coulomb integrals, which is the most time consuming part of the computation, can be stored in RAM (random access memory), whereas the angular parts that consist of much simpler algebraic expressions, can be evaluated on the fly.

In our calculations we made use of the CCSD-EPC approximation,[8] which reduces the number of cluster amplitudes by a factor of 2. Ideally, the two-body cluster amplitudes $(T_2 = \langle pq|t_2^k|ab\rangle)$ can have any multipole moments k that satisfies

$$|l_p - l_a| \leq k \leq |l_a + l_p| \quad |l_q - l_b| \leq k \leq |l_q + l_b|, \tag{2.12}$$

and

$$(-)^{l_a + l_p} = (-)^{l_q + l_b}. \tag{2.13}$$

The Coulomb matrix element $\langle pq|V^k|ab\rangle$ is, however, only nonzero if

$$l_p + l_a + k = \text{even}, \quad l_q + l_b + k = \text{even} \tag{2.14}$$

in addition to the conditions given in Eqs. (2.12)–(2.13). Therefore, according to MBPT the two-body cluster amplitudes satisfying Coulomb selection rules are only nonzero at the first order (in Coulomb) level. The remaining two-body cluster amplitudes are zero at the first order level but nonzero at higher order level. It can easily be shown that Coulomb allowed two-body cluster amplitudes are evenly spaced, i.e., these are either 0, 2, 4, etc. or 1, 3, 5, etc. We call the Coulomb allowed two-body cluster amplitudes as even-parity channel or EPC and Coulomb rule violating two-body cluster amplitudes as odd-parity channel or OPC. It immediately follows from the above argument that the number of two-body cluster operator in EPC approximation is roughly half of the all-parity channels or APC (EPC+OPC).

Since the ground state of alkali metal atoms contains only one electron in its outermost occupied s orbital, the ground and excited state energies (also the properties) can be conveniently computed through the Fock-space-relativistic coupled cluster method. In this method, the Dirac–Fock–Coulomb (DFC) equations are solved for the positive ion M^+ which defines the $(0h,0p)$ valence sector. [Note that (mh,np) valence sector corresponds to the set of all excited $(N-m+n)$ electron determinants with m hole and n particle occupancies in the active hole, particle orbitals.] The ion is then correlated by CCSD and one electron is then added, following the Fock-space scheme,[9]

$$M^+(0,0)+e \rightarrow M(0,1). \tag{2.15}$$

When the valence electron is attached to the first unoccupied s orbital of the ion (M^+) we get the ground state of M. Similarly, the valence electron can be attached to any arbitrary virtual orbital to obtain the excited states of M. In order to add an electron to the kth virtual orbital of the DF reference state, we define

$$|\Phi_k^{n+1}\rangle \equiv a_k^\dagger |\Phi\rangle \tag{2.16}$$

with the help of the particle creation operator $a_k^\dagger$. We now define the exact state using excitation operators for both, the core electrons and the valence electron, in the following way:

$$|\Psi_k^{n+1}\rangle = e^T \{e^{S_k}\}|\Phi_k^{n+1}\rangle, \tag{2.17}$$

where $\{S_k\}$ is the normal ordered valence electron excitation operator.[10] Since S_k has to contain the particle annihilation operator a_k, it cannot, due to the normal ordering, be connected with any other valence electron excitation operator $\{S_k\}$ so that $\{e^{S_k}\}$ reduces to $(1+S_k)$ and we can rewrite Eq. (2.17) as

$$|\Psi_k^{n+1}\rangle = e^T(1+S_k)|\Phi_k^{n+1}\rangle. \tag{2.18}$$

Following the same procedure as in the closed shell approach, we obtain a set of equations

$$\langle \Phi_k^{n+1}|\bar{H}(1+S_k)|\Phi_k^{n+1}\rangle = \Delta E_k \equiv H_{\mathrm{eff}}, \tag{2.19}$$

and

$$\langle \Phi_k^{*,n+1}|\bar{H}(1+S_k)|\Phi_k^{n+1}\rangle = \langle \Phi_k^{*,n+1}|S_k|\Phi_k^{n+1}\rangle \Delta E_k. \tag{2.20}$$

Here, ΔE_k is the difference between the energy of the closed shell state Ψ and the single valence state Ψ_k^{n+1}, i.e., the energy which is released when an electron is attached to the kth virtual orbital of the closed shell state. Equation (2.20) is nonlinear in S_k because the energy difference ΔE_k itself is a function of S_k. The S_k amplitude determining equations are solved in a self-consistent way where process begins with an initial guess for the S_k amplitudes, e.g., $S_k=0$, evaluate the energy difference using Eq. (2.19). With the updated ΔE_k, Eq. (2.20) is solved to determine the S_k amplitudes and the process is iterated until S_k amplitudes converges.

Since the full couple cluster with singles, double, and triples (CCSDT) is computationally expensive, the effect of triples is included in the open-shell CC equations in an approximate way,

$$S_{abk}^{pqr} = \frac{\widehat{VT}_2 + \widehat{VS}_2}{\epsilon_a + \epsilon_b + \epsilon_k - \epsilon_p - \epsilon_q - \epsilon_r}, \tag{2.21}$$

where S_{abk}^{pqr} are the amplitudes corresponding to the simultaneous excitation of orbitals a, b, k to p, q, r; $\widehat{VT}$, $\widehat{VS}$ are the contraction of all creation/annihilation operators; and ϵ_i is the orbital energy of the ith orbital. This contribution is added to the energy obtained using singles and doubles. However, the contribution of triples can be incorporated in the CC computations in two ways. The simplest and inexpensive approach is the inclusion of the lowest order contribution of triples of H_{eff} through the converged T and S cluster amplitudes. In this approach S_{abk}^{pqr} is not coupled to one and two-body S-amplitudes. Following the notations of Kaldor[11] and Bartlett,[12,13] this scheme is called CCSD/LCCSD+T. Alternatively, the effect of triples can be incorporated in the CC equations through the *back coupling* of triples to one and two-body S-amplitudes via ΔE_k. This scheme is known as CCSD(T)/LCCSD(T).[12,13]

III. COMPUTATION

The Fock-space relativistic coupled cluster method is applied to compute the ground and excited state energies of Rb and Cs. The Dirac–Fock equations are first solved for the alkali metal ion M^+, which defines the (0-hole, 0-particle) sector of the Fock space. The ion is then correlated using the closed shell CCSD/LCCSD, after which one-electron is added following the Fock-space scheme:

$$M^+(0,0) \rightarrow M(0,1).$$

Both the DF and relativistic CC programs utilize the angular momentum decomposition of the wave functions and CC equations. Using the Jucys–Levinson–Vanagas theorem,[14] the Goldstone diagrams are expressed as a products of angular momentum diagrams and reduced matrix element. This procedure simplifies the computational complexity of the DF and relativistic CC equations. Appropriate constraints are also imposed to avoid "variational collapse" and "continuum dissolution."

In the actual computation, the DF ground state and excited state properties of Rb and Cs are computed using the finite basis set expansion method (FBSE) (Ref. 15) with a large basis set of $(34s\,30p\,20d\,15f)$ Gaussian functions of the form,

$$F_{i,k}(r) = r^k \cdot e^{-\alpha_i r^2} \tag{3.1}$$

TABLE I. Comparison of valence electron removal energies (in cm^{-1}) of rubidium obtained from APC and EPC coupled cluster method (CCM) with all active and frozen core (Ne-core) orbital calculations.

| | All-core | Ne-core | |
| | | | |
Orbital	CCSD-APC	CCSD-APC	CCSD-EPC
$5s$	33558.88	33563.59	33559.80
$5p_{1/2}$	21016.47	21017.71	21016.01
$5p_{3/2}$	20780.17	20781.59	20779.75
$6s$	13495.87	13495.46	13495.25
$6p_{1/2}$	9922.08	9922.48	9922.16
$6p_{3/2}$	9843.28	9843.75	9843.35

TABLE II. Comparison of valence electron removal energies (in cm^{-1}) of cesium obtained from APC and EPC coupled cluster method (CCM) with frozen core (Ne-core) orbitals calculations.

Orbital	Ne-core	
	CCSD-APC	CCSD-EPC
$6s$	31275.11	31275.24
$6p_{1/2}$	20114.71	20114.23
$6p_{3/2}$	19570.61	19570.55
$7s$	12809.71	12810.89
$7p_{1/2}$	9570.19	9570.71
$7p_{3/2}$	9382.45	9382.94

TABLE IV. Percentage of error (absolute) in the estimation of valence electron removal energies of rubidium using the coupled cluster method (CCM).

Orbital	CCSD(T)	CCSD	LCCSD	LCCSD(T)	Safronova *et al.*[a]	Eliav *et al.*[b]
$5s$	0.240	0.377	0.131	0.003	0.125	0.089
$5p_{1/2}$	0.152	0.469	0.341	0.043	0.000	0.023
$5p_{3/2}$	0.206	0.467	0.426	0.187	0.000	0.019
$6s$	0.089	0.457	0.390	0.000	0.221	0.052
$6p_{1/2}$	0.020	0.551	0.511	0.000	0.070	1.193
$6p_{3/2}$	0.081	0.586	0.535	0.061	0.061	1.313
Average Error	0.131	0.484	0.389	0.049	0.080	0.448

[a]Reference 6.
[b]Reference 7.

with $k=0,1,...$ for s, $p,...$ type functions, respectively. For the exponents, the even tempering condition

$$\alpha_i = \alpha_0 \beta^{i-1} \tag{3.2}$$

is applied. Here, N is the number of basis functions for a specific symmetry. The self-consistent DF orbitals are stored on a grid. It is assumed that virtual orbitals with high energies do not contribute significantly to properties like IPs. In the CCSD calculations, we therefore truncate the virtual orbital space above a certain threshold.

The ground and excited state properties of Rb are computed with two sets of basis functions with $\alpha_0 = 0.00525$ and $\beta = 2.73$. While the first set consists of $12s$, $11p$, $9d$, and $5f$ active orbitals, the second set consists of $13s$, $12p$, $10d$, and $5f$ active orbitals. [The unoccupied orbitals with orbital energy above 1500 a.u. (for s and p) and 200 a.u. (for d) are not included in the CC calculations.] To examine the core effects on the IPs, two sets of calculations are performed. In the first set all occupied orbitals are kept active and in the second set $1s$, $2s$, and $2p$ are kept frozen (*frozen Ne-core*), i.e., excitations out these orbitals are absent in the T and S amplitude determining CC equations. Similarly, to estimate the contribution of the odd-parity channel cluster (OPC) amplitudes to the ground state and excited/ionized state energies, we compute the ground and excited state energy levels of Rb using Fock-space CC equations with *even-parity* and *all-parity* channel cluster amplitudes.

IV. RESULTS AND DISCUSSIONS

Table I collects the valence electron removal energies of Rb obtained from all core computations (with $12s11p9d5f$ active orbitals) and the corresponding results obtained with a frozen Ne-core. Whereas the $5s$ level energy changes by little more than 0.01%, the other ones remain practically unchanged. These numbers justify the approach to freeze inner core orbitals for excitation energy studies, as carried out in earlier works.[11] For the frozen Ne-core, a computation using the EPC approximation is added (column 4). Again, the changes are of the order of 0.01% and therefore of no relevance even for ambitious projects. Because of the Coulomb selection rule, the first order OPC amplitudes are zero, and, hence their contribution to the second order state energy is also zero. This explains why the contribution of OPC amplitudes to the ground and excited state energies is negligibly small. The results displayed in Table II prove that the same holds for Cs. The EPC approximation, although taking only one half of the computation time, leads to results that differ by less than 0.01% compared to the more complete APC scheme.

Table III reports the valence electron removal energies of Rb obtained from CC theory with the experiment[16] and with other theoretical calculations. The computed quantities displayed in Tables III–VI are obtained from $13s12p10d5f$ active orbitals EPC-CC calculations with all active core. A

TABLE III. Valence electron removal energies (in cm^{-1}) of rubidium obtained from the coupled cluster method (CCM) with even-parity channels.

Method	$5s$	$5p_{1/2}$	$5p_{3/2}$	$6s$	$6p_{1/2}$	$6p_{3/2}$
LCCSD	33647	21040	20785	13504	9925	9846
LCCSD+T	33690	21105	20837	13557	9977	9894
LCCSD(T)	33690	21103	20835	13557	9976	9893
CCSD	33563	21013	20777	13495	9921	9841
CCSD+T	33603	21080	20831	13546	9974	9891
CCSD(T)	33603	21080	20831	13545	9974	9891
Safronova *et al.*[a]	33649	21111	20875	13527	9969	9893
Eliav *et al.*[b]	33721	21117	20878	13564	9857	9769
Experiment[c]	33691	21112	20874	13557	9976	9899

[a]Reference 6.
[b]Reference 7.
[c]Reference 16.

TABLE V. Valence electron removal energies (in cm^{-1}) of cesium obtained from the coupled cluster method (CCM) with even-parity channels.

Method	$6s$	$6p_{1/2}$	$6p_{3/2}$	$7s$	$7p_{1/2}$	$7p_{3/2}$
LCCSD	31485	20191	19637	12858	9592	9402
LCCSD+T	31382	20187	19616	12880	9622	9425
LCCSD(T)	31381	20186	19615	12878	9620	9424
CCSD	31358	20139	19590	12830	9580	9390
CCSD+T	31252	20136	19573	12848	9610	9413
CCSD(T)	31250	20137	19574	12848	9609	9413
Safronova *et al.*[a]	31262	20204	19652	12801	9621	9442
Eliav *et al.*[b]	31442	20224	19662	12876	9552	9354
Blundell *et al.*[c]	31291	20187	19645	12828	9623	9443
Experiment[d]	31407	20229	19674	12872	9641	9459

[a]Reference 6.
[b]Reference 7.
[c]Reference 4.
[d]Reference 16.

TABLE VI. Error in valence electron removal energy computations of cesium using the coupled cluster method. (Value within parentheses are obtained from the CCSD+T/LCCSD+T scheme.)

Orbital	CCSD(T)	CCSD	LCCSD	LCCSD(T)	Blundell et al.[a]	Safronova et al.[b]	Eliav et al.[c]
$6s$	0.500(0.494)	0.156	0.248	0.083(0.080)	0.369	0.462	0.114
$6p_{1/2}$	0.455(0.455)	0.445	0.188	0.213(0.208)	0.208	0.124	0.025
$6p_{3/2}$	0.508(0.513)	0.429	0.188	0.298(0.294)	0.147	0.112	0.061
$7s$	0.186(0.186)	0.326	0.109	0.047(0.062)	0.342	0.552	0.031
$7p_{1/2}$	0.322(0.322)	0.633	0.508	0.218(0.197)	0.187	0.207	0.923
$7p_{3/2}$	0.486(0.486)	0.729	0.603	0.370(0.359)	0.169	0.180	1.110
Average Error	0.409(0.410)	0.453	0.307	0.205(0.200)	0.237	0.273	0.377

[a]Reference 4.
[b]Reference 6.
[c]Reference 7.

similar basis is also applied for Cs but with a little more active orbitals ($13s12p10d7f$). While Table V compares the calculated valence electron removal energies of Cs with the experiment[16] and with other theoretical results, Table VI collects the error in the estimated quantities. The present calculations clearly show that triples excitations contribute substantially to the estimated state energy. For instance, the inclusion of partial triples improves the accuracy of the estimated state energy of Rb and Cs by 0.35% and 0.20%, respectively (see Tables IV and VI). The present as well as the previous theoretical calculations suggest that the linearized CC fares better than CC. In fact, our LCCSD(T) results for both, Cs and Rb, are closer to the experiment than any other computation presented so far, including our own CCSD(T) results. However, this is likely to be a spurious effect, because CCSD/CCSD(T) is theoretically more accurate than its linearized version. The cumulative contributions of higher order excitations in the CC scheme, as well as Breit and QED effects are expected to improve the accuracy of CCSD(T) compared to its linearized version. More detailed investigation of this point is therefore necessary and research in this direction is in progress.

V. CONCLUDING REMARKS

The relativistic open-shell coupled cluster scheme for direct energy difference calculations is presented and applied to Rb and Cs atoms. In this work, we investigate the effects of electron correlations on the ground and excited state properties using different levels of CC approximations. We have shown that neither the freezing of inner core orbitals (Ne-core) nor the neglection of odd-parity channel amplitudes alter the results by more than about 0.01%. At least for this type of systems and the properties under investigation, there

is no objection against an implementation of these approximations which can save a significant amount of computational effort.

Satisfactory results are obtained for the valence electron ionization potentials. Our LCCSD(T) results differ by 0.05% (Rb) and 0.2% (Cs) from the experiments and are therefore closer than earlier works. It is remarkable that higher level CCSD(T) approximation leads in average to less accurate numbers.

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