Relativistic coupled-cluster-based linear response theory for ionization potentials of alkali-metal and alkaline-earth-metal atoms

Rajat K. Chaudhuri, Prafulla K. Panda, and B. P. Das
NAPP Group, Indian Institute of Astrophysics, Bangalore 560034, India

Uttam Sinha Mahapatra and D. Mukherjee
Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India
(Received 25 January 1999)

We have developed and applied the relativistic coupled-cluster-based linear response theory (RCCLRT) for computing the principal as well as the shake-up ionization potentials (IP's) of Li, Be, Na, and Mg where the single-particle orbitals are generated by solving the relativistic Hartree-Fock-Roothaan equations using the Gaussian basis functions on a grid. The computed principal and shake-up ionization energies by the RCCLRT approach are in favorable agreement with the experimental results. Since for the (one-valence) IP problem, there is a formal equivalence between the principal IP values as obtained from the CCLRT and those obtained as eigenvalues of the multireference coupled-cluster theory, the computed quantities are fully size extensive. The approach via the RCCLRT has the additional advantage of providing the shake-up IP's as well. These are, however, not fully size extensive, but the error scales as the number of valence excitations ($2h$-$1p$), so the inextensivity error is rather small. [S1050-2947(99)01907-1]

PACS number(s): 31.15.Dv

I. INTRODUCTION

It is now widely recognized that the coupled-cluster (CC) methodology [1–12] is one of the most powerful nonperturbative techniques for studying the electronic structure of atoms and molecules. It has been applied with great success to a wide variety of problems involving a host of atomic and molecular systems. The cluster expansion of the wave function in the CC approach provides, in a straightforward manner, the size extensivity of the computed energies. (In many-body parlance, the term size extensivity implies that the energy expression must consist of connected quantities. When this is satisfied, the theory is called size extensive [2].) However, it is rather surprising that while the coupled-cluster methods have been extensively applied to a wide variety of nonrelativistic atomic and molecular systems (ranging from helium to free base porphin [13]), only a few attempts have been made to extend them to the relativistic regime. This is due largely to the fact that the relativistic one-particle spinors obtained from the self-consistent Dirac-Fock equations are numerous and consequently the post-Dirac-Fock applications using those spinors are computationally more time consuming than those in the nonrelativistic case. In addition, there is the occurrence of *variational collapse* or bound failure in the relativistic self-consistent field equations with the attendant *continuum dissolution* [14]. This makes post-Hartree-Fock calculations using either the perturbative or nonperturbative expansion somewhat problematic from a formal point of view. Prompted by the initial success on the bound failure problem with the finite basis methods, considerable progress has been made in solving the relativistic self-consistent field equation for many-electron systems using the finite basis method, and, in recent years, there has been an increased interest in the application of many-body perturbation theory (MBPT) and coupled-cluster methods to relativistic atomic and molecular systems [15–20] where the problem of continuum dissolution is formally avoided by introducing suitable projection operators [14].

In this paper, we report the results of our calculation for principal as well as shake-up ionization potentials of Li, Be, Na, and Mg using the coupled-cluster-based linear response theory (CCLRT) [21–27] as extended to handle relativistic systems (RCCLRT). We have used a kinetically balanced finite Gaussian basis set expansion (FBSE) to represent occupied and virtual orbitals. Recently, we have developed a hybrid technique to solve the atomic relativistic self-consistent field (SCF) equations using a finite basis (kinetically balanced) expansion method [28]. While the numerical Dirac-Fock (DF) calculations are more compact and accurate than the FBSE approach, the latter has some distinct advantages over the former. First of all, the accuracy of the total energy and wave function obtained through the Dirac-Fock-Roothaan equation (relativistic SCF as in the FBSE approach) can, *in principle*, be enhanced to any degree by increasing the number of basis functions, and, secondly, the generation of the occupied and virtual orbitals does not require separate computations. It has been found that the numerical wave functions [29] provide a more accurate description of the orbitals in the asymptotic region than the analytical ones (using the FBSE approach), but on the other hand, the FBSE approach is more convenient for generating the orbitals. This indicates that an appropriate combination of these two approaches can be profitably used to generate the single-particle spinors from a single computation. In our hybrid method, the atomic orbitals are expanded in terms of the basis functions where the latter are defined on a grid, but the one- and two-electron radial integrals appearing in the Dirac-Fock-Roothaan matrix are evaluated numerically as opposed to the conventional Dirac-Fock-Roothaan approach [28]. The hybrid scheme is also numerically efficient because it can provide an easy route to the implementation of $2 \times N_c$ operations (both the direct and exchange two-electron

integral evaluations involve N_c operations and need to be computed separately in our approach) rather than $N^2 \times N_c$ operations in the evaluation of two-electron integrals (Dirac-Fock potential term) in DF-SCF equations. (Here, N and N_c denote the number of basis functions and occupied orbitals, respectively.)

For computing the energy differences of spectroscopic interest through the CC method, one has two options to choose depending upon the type of extensivity that one wishes to ensure on the computed energies. For instance, starting with a certain model of space functions of partial hole-particle occupancy, one may generate a full cluster expansion involving all possible cluster excitations from the ''core'' (doubly occupied part of the model space functions) as well as from the ''valence'' (partially occupied part of the model functions) orbitals. The CC theory that uses the full cluster expansions of this type is called the ''core-valence'' extensive CC theory because it ensures the extensivity of the computed energies with respect to the core as well as the valence electrons separately. What this essentially means is the following: the total energy of an excited/ionized state E_k is additively separable to a sum of the ground state energy E_0 and the energy differences ΔE_k, where both the ground state and energy differences are computed in a size-extensive manner with respect to all electrons. (Note that as above, an alternative CC approach is also in use, where extensivity of the computed energies is maintained with respect to all the electrons without dissecting it into core and valence separately [11].) Here, one may argue that since the bulk contribution to E_k comes from the ground state energy E_0, with ΔE_k only a small component, it would suffice to compute the ground state energy E_0 in a completely size-extensive manner and treat ΔE_k in a size-inextensive manner. The difference in energies computed in this fashion will then be size inextensive only with respect to partial valence occupancies. If the number of valence occupancies is small compared to the doubly occupied orbital, then the computed energy differences will have rather small size-inextensive error [30]. The core-extensive CC theories of this type are characterized by the presence of the CC form for the ground state wave function and the configuration interaction (CI) form for the valence correlation part in the description of the excited/ionized states. It should be emphasized that although the core-extensive and core-valence-extensive CC theories are formally equivalent for single-valence systems, i.e., for electron attachment (EA) and detachment processes [ionization potentials (IP)], CCLRT has some distinct advantages over the core-valence open-shell CC theory. Being an eigenvalue equation, CCLRT does not suffer from convergence problems like the core-valence-extensive open-shell CC method and provides all the desired roots including the valence ionization energies as well as ionization energies for the shake-up states in a one shot. The ionization energies for shake-up states (generally called the satellite energies) are important in the sense that it provides a better description of the experimental photoionization spectra. It is worthwhile to mention that when the dimension of the CCLRT matrix for IP/EA becomes too large or if all the roots are not required, then it is computationally simpler to compute the IP/EA values through the multireference CC method (MRCC).

Coupled-cluster-based linear response theories (also known as equation of motion CC or EOM-CC) [21–27] and the closely related formalism called symmetry adapted cluster configuration interaction (SAC-CI) [31] are typical examples of core-extensive CC formulations for energy differences. [The SAC-CI is a theory for the excited states. In this method the excited state configuration state functions (CSFs) are generated by the action of a suitable excitation operator on the ground state wave function where the latter is obtained by the action symmetry adapted cluster operator on the unperturbed ground state CSF.] Both time-dependent [21] and time-independent [22] CCLRT formulations have been developed for the energy difference computations of which the latter provides a more direct formulation as eigenvalue equations for ΔE_k. There are yet no CCLRT applications for energy difference calculations where relativistic effects are important. The full cluster expansion of the core-valence extensive variety was, however, applied in computing the ionization energies of relativistically important systems some years ago [15–20].

In this paper, we present the ionization potentials and excitation energies (EE) (obtained as a by-product) of alkali-metal and alkaline-earth-metal atoms computed through the CC approach using the relativistic wave functions generated through the hybrid DF-SCF approach. Since the electron correlation is significant for the alkaline-earth-metal atoms compared to the alkali-metal atoms, the computations of transition energies for the former will provide a more stringent test of the quality of the single-particle orbitals generated through the hybrid DF-SCF method. The second motivation of this work is to improve the accuracy of the theoretically computed transition energies of these systems.

The present work demonstrates that RCCLRT not only produces highly accurate ionization energies but also a precise estimation of transition energies. It also highlights the importance of the electron correlation in the computation of ionization and transition energies. However, since the systems studied here are neither heavy nor highly stripped, no attempts have been made to quantify the relativistic effect. Work in this direction is in progress.

Section II begins with a brief review of the CCLRT method for computing energy differences. The generation of single-particle orbitals through DF-SCF and computational details along with the numerical results are described in Secs. III and IV, respectively.

II. CCLRT FOR ENERGY DIFFERENCE CALCULATIONS

Since the basic formalism of the time-independent version of the CCLRT is available elsewhere [22–26], we only present a general overview of that approach. Let us assume that we have already solved for the N-electron ground state Ψ_0, dominated by the closed-shell single reference Hartree-Fock function Φ_0 via the single reference CC theory (SRCC) [1,2]:

$$|\Psi_0\rangle = \exp(T)|\Phi_0\rangle, \qquad (2.1)$$

where $\exp(T)$ is the CC representation of the wave operator for the ground state. The cluster operator T consists of various $np\text{-}nh$ excitations T_n from the particle-hole vacuum state Φ_0. The cluster amplitudes of various $np\text{-}nh$ excita-

tions are found in SRCC theory by equating np-nh amplitudes of the transformed Hamiltonian $\exp(-T)H\exp(T)$ to zero, i.e.,

$$\langle\Phi_i^{n,n}|\exp(-T)H\exp(T)|\Phi_0\rangle=0, \qquad (2.2)$$

where $|\Phi_i^{n,n}\rangle$'s are various np-nh excited determinants. Here, np and nh stand for the number of particle creation and hole annihilation operators acting on the reference determinant.

In CCLRT formalism, an $(N+N_e)$-electron excited/ionized state is represented as

$$|\Psi_k\rangle=W_k^\dagger\exp(T)|\Phi_0\rangle, \qquad (2.3)$$

where $W_k^\dagger$ is an excitation/ionization operator creating the kth $(N+N_e)$-electron state of interest. $W_k^\dagger$ consists of various mp-nh ($m-n=N_e$) excitation operators which create mp-nh excited states out of Φ_0. Clearly, $N_e=-1$ for ionization process, and, hence $W_k^\dagger$ should contain mp-nh excitation operators with $m-n=-1$.

Using the equation of motion form for E_k (that is why CCLRT is also termed as EOM-CC), the relevant equations for the difference energy calculation can be written as

$$[H,W_k^\dagger]\exp(T)|\Phi_0\rangle=\Delta E_k W_k^\dagger\exp(T)|\Phi_0\rangle. \qquad (2.4)$$

Since $W_k^\dagger$ and $\exp(T)$ commute, premultiplying Eq. (2.4) by $\exp(-T)$ and commuting $\exp(T)$ against $W_k^\dagger$ we get

$$[\tilde{H},W_k^\dagger]|\Phi_0\rangle=\Delta E_k W_k^\dagger|\Phi_0\rangle, \qquad (2.5)$$

where

$$\tilde{H}=\exp(-T)H\exp(T). \qquad (2.6)$$

Introducing the dressed Hamiltonian $\hat{H}$ by the relation

$$\exp(-T)H\exp(T)=\hat{H}+E_{\mathrm{gr}}, \qquad (2.7)$$

where E_{gr} is the number component of $\tilde{H}$ and $\hat{H}$ contains the operator components of $\tilde{H}$, we obtain

$$[\hat{H},W_k^\dagger]|\Phi_0\rangle=\Delta E_k W_k^\dagger|\Phi_0\rangle, \qquad (2.8)$$

where $\Delta E_k=E_k-E_{\mathrm{gr}}$.

Let us now define the composite $W_k^\dagger$ in terms of various mp-nh components as

$$W_k^\dagger=\sum_{m,n}W_k^{\dagger m,n}, \qquad (2.9)$$

with

$$W_k^{\dagger m,n}=\sum_i C_{k,i}^{m,n}Z_i^{\dagger m,n}, \qquad (2.10)$$

where $C_{k,i}^{m,n}$ are the various ith component of the mp-nh excitations and $Z_i^{\dagger m,n}$ are products of the mp-nh creation operators. Substituting Eq. (2.9) [along with Eq. (2.10)] into Eq. (2.8) we get

$$\sum_{r,s}\sum_j\langle\Phi_i^{m,n}|[\hat{H},Z_j^{\dagger r,s}]|\Phi_0\rangle C_{k,j}^{r,s}=\Delta E_k C_{k,i}^{m,n}. \qquad (2.11)$$

Since the various mp-nh amplitudes of the ground state cluster components T_n have been evaluated by equating np-nh amplitudes of $\tilde{H}$ in the CC theory, $\hat{H}|\Phi_0\rangle=0$ and, hence, Eq. (2.11) can be rewritten as

$$\sum_{r,s}\sum_j\langle\Phi_i^{m,n}|\hat{H}|\Phi_j^{r,s}\rangle C_{k,j}^{r,s}=\Delta E_k C_{k,i}^{m,n}. \qquad (2.12)$$

Equation (2.12) constitutes the CCLRT equation for the $(N+N_e)$ excited/ionized states. Once the matrix elements of $\hat{H}$ are constructed from the matrix elements of H and T, the computation of the energy differences ΔE_k boiled down to the diagonalization of the matrix $R_{i,j}^{m,n;r,s}\equiv\langle\Phi_i^{m,n}|\hat{H}|\Phi_j^{r,s}\rangle$. Since $\hat{H}$ is obtained via a similarity transformation, the matrix elements of $\hat{H}$ are non-Hermitian and, therefore, matrix R is also non-Hermitian.

For practical purpose, it is absolutely necessary to truncate both T_n and $W_k^\dagger$ after some np-nh and mp-nh rank and the most widely used truncation schemes for T and $W_k^\dagger$ (for IP) are

$$T=T_1+T_2, \qquad W_k^\dagger=W_k^{\dagger 0,1}+W_k^{\dagger 1,2}. \qquad (2.13)$$

III. COMPUTATIONAL DETAIL

Generation of basis and integrals

In the realm of the relativistic many-body problem, we start from the Dirac-Coulomb Hamiltonian that can be conveniently written as

$$H=\sum_{i=1}^N\left[c\vec{\alpha}_i\cdot\vec{p}_i+(\beta_i-1)mc^2+V_{\mathrm{nuc}}(r_i)\right]+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}, \qquad (3.1)$$

in which the Dirac operators $\vec{\alpha}$ and β are expressed in terms of Pauli matrices and I is the 2×2 unit matrix.

In the central field approximation, the SCF equations are determined by minimizing the energy functional E with respect to Φ, where E is given by

$$E=\left\langle\Phi\left|\sum_{i=1}^N\left[c\vec{\alpha}_i\cdot\vec{p}_i+(\beta_i-1)mc^2+V_{\mathrm{nuc}}(r_i)\right]\right.\right.$$
$$\left.\left.+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\right|\Phi\right\rangle, \qquad (3.2)$$

and determinantal wave function (antisymmetric) u is built from single-particle orbitals

$$u(r,\theta,\phi)=\begin{pmatrix}r^{-1}P_{n\kappa}(r)\chi_{\kappa m}(\theta,\phi)\\ir^{-1}Q_{n\kappa}(r)\chi_{-\kappa m}(\theta,\phi)\end{pmatrix}, \qquad (3.3)$$

where $r^{-1}P_{n\kappa}(r)$ and $r^{-1}Q_{n\kappa}(r)$ are the large and small component radial wave functions, respectively, that satisfy the orthonormality condition

$$\int_0^\infty dr[P_{n\kappa}(r)P_{n'\kappa}(r)+Q_{n\kappa}(r)Q_{n'\kappa}(r)]=\delta_{nn'} . \quad (3.4)$$

Here, the quantum number κ classifies the orbital according to its symmetry and is given by

$$\kappa=-2(j-l)\left(j+\frac{1}{2}\right), \quad (3.5)$$

where l is the orbital quantum number and $j=l\pm\frac{1}{2}$ is the total angular quantum number. Here, the spinors $\chi_{\kappa m}(\theta,\phi)$ are given by

$$\chi_{\kappa m}=\sum_{\sigma\pm\frac{1}{2}} C\left(l\frac{1}{2}j;m-\sigma,\sigma\right)Y_{l,m-\sigma}(\theta,\phi)\eta_\sigma, \quad (3.6)$$

where $C(l\frac{1}{2}j;m-\sigma,\sigma)$ and $Y_{l,m-\sigma}(\theta,\phi)$ represent the Clebsch-Gordan coefficients and the normalized spherical harmonics, respectively, and the η_σ stands for the two-component spinors.

Now, it has been found that the numerical wave functions have more accurate asymptotic behavior than the analytical ones, though both provide total energies of comparable accuracy. The accuracy of the total energy and wave function obtained through the Dirac-Fock-Roothaan equation (FBSE method) can *in principle* be enhanced to any degree by increasing the number of basis functions, but *in reality* only a finite number of bases can be used because the computational time increases very rapidly with the increasing number of basis functions. Moreover, the use of large basis functions severely impedes the efficiency of the post-Dirac-Fock computations.

In the present paper, we use a hybrid scheme developed recently by us [28] to solve the DF equation through the pseudoeigenvalue approach where basis functions are defined on a grid and one- and two-electron radial integrals are evaluated numerically as opposed to the conventional relativistic Hartree-Fock-Roothaan equations. Since the basis functions are defined on a grid and the matrix elements appearing in the relativistic Hartree-Fock-Roothaan equations are evaluated numerically, this scheme can be regarded as a combination of numerical and analytical approach to the solution of DF-SCF equation. Here, like the traditional analytical basis set expansion approach, the large and small components of the radial wave functions are expressed as linear combination of basis functions, i.e.,

$$P_{n\kappa}(r)=\sum_p C_{\kappa p}^L g_{\kappa p}^L(r), \quad (3.7)$$

and

$$Q_{n\kappa}(r)=\sum_p C_{\kappa p}^S g_{\kappa p}^S(r), \quad (3.8)$$

where the summation index p runs over the number of basis functions N, $g_{\kappa p}^L(r)$, and $g_{\kappa p}^S(r)$ are basis functions belonging to the large and small components, respectively, and $C_{\kappa p}^L$ and $C_{\kappa p}^S$ are the corresponding expansion coefficients.

Though any basis functions can be used, we have chosen Gaussian-type orbitals (GTOs) that have the following form for the large component:

$$g_{\kappa p}^L(r)=\mathcal{N}_p^L r^{n_\kappa}e^{-\alpha_p r^2}, \quad (3.9)$$

with

$$\alpha_p=\alpha_0\beta^{p-1}, \quad (3.10)$$

where α_0,β are user defined constants, n_κ specifies the orbital symmetry (1 for s, 2 for p, etc.) and $\mathcal{N}_p^L$ is the normalization factor for the large component. The small component part of the basis function is obtained by imposing the kinetic balance and has the form

$$g_{\kappa p}^S(r)=\mathcal{N}_p^S\left(\frac{d}{dr}+\frac{\kappa}{r}\right)g_{\kappa p}^L(r), \quad (3.11)$$

where

$$\mathcal{N}_p^S=\sqrt{\frac{\alpha_p}{2n_\kappa-1}[4(\kappa^2+\kappa+n_\kappa)-1]}. \quad (3.12)$$

The imposition of kinetic balance on the small component through Eq. (3.11) allows us to use the same set of exponents for the large and small component, and hence reduces the computational costs. Moreover, Dyall, Grant, and Wilson [34] and Stanton and Havriliak [35] show that using the relation (3.11) the computed kinetic energy approaches smoothly to the nonrelativistic limit when the light velocity $c\to\infty$. It has also been shown by Stanton and Havriliak that the calculated energy can fall below the exact energy by an amount of the order of $1/c^4$ but the error disappears as the basis becomes complete. The imposition of kinetic balance condition on the small component also provides a better behavior of the energy functional for determining the orbitals and their energies.

In the SCF procedure, the integrals and the matrices are evaluated over the members of the basis set $\{\phi_\mu\}$ rather than over the members of the set of solutions $\{\psi_i\}$ because the atomic or molecular orbitals (solutions of SCF equations) are not known until the calculation is complete. Since these two sets of functions are related by

$$\psi_i=\sum_{\mu=1}^N C_{\mu i}\phi_\mu, \quad (3.13)$$

the two-electron matrix element of F (the Hartree-Fock potential term) in $\{\phi\}$ basis can be written as

$$U_{ij}=\sum_c \left\langle \phi_i\psi_c \left| \frac{1}{r_{12}} \right| \phi_j\psi_c \right\rangle$$

$$\equiv\sum_c \sum_\mu \sum_\nu C_{\mu c}^* C_{\nu c}\left\langle \phi_i\phi_\mu \left| \frac{1}{r_{12}} \right| \phi_j\phi_\nu \right\rangle, \quad (3.14)$$

which involves a two-index transformation. However, this two-index transformation process can be easily avoided by evaluating the U_{ij} matrix elements in a mixed basis, i.e., in $\{\phi,\psi\}$ basis. This is trivial, because the occupied orbitals can be updated (like the density matrix) during the SCF iteration

TABLE I. First and second ionization potential (in eV) of alkali-earth metals.

Atom	Ionizing orbital	Koopmans' IP	MBPT(2)	CCLRT	Experiment [a]
Li	$2s_{1/2}$	5.342	5.386	5.392	5.392
	$3s_{1/2}$	2.005	2.015	2.016	2.019
	$2p_{1/2}$	3.500	3.536	3.538	3.544
	$2p_{3/2}$	3.500	3.536	3.535	3.544
Na	$3s_{1/2}$	4.954	5.105	5.138	5.139
	$4s_{1/2}$	1.906	1.938	1.941	1.948
	$3p_{1/2}$	2.979	3.025	3.049	3.037
	$3p_{3/2}$	2.977	3.022	3.043	3.035

[a]Reference [33].

and, therefore, the two-electron matrix element $\langle \phi_i \psi_c | (1/r_{12}) | \phi_j \psi_c \rangle$ can be directly computed at each iteration without invoking the two-index transformation.

IV. APPLICATIONS

We employ an uncontracted Gaussian basis that ranges from $15s12p10d$ (for lithium) to $22s20p15d5f$ (for magnesium) for computing the ionization potentials of Li, Be, Na, and Mg through the coupled-cluster-based linear response theory.

Table I compares our CCLRT calculation of the valence ionization energies of Li, Be, Na, and Mg atoms with the experiment and with other available *ab initio* works that roughly consider the same number of active orbitals. There are a few interesting features that we would like to highlight here. First of all, we find from Table I that the accuracy of the ionization potentials estimated through Koopmans' theorem (KT) [32] and the second order MBPT decrease with increasing atomic number. We also observed a similar trend while computing the second order IP across the periodic table. In fact, this is quite expected because the second order MBPT (Möller-Plesset) inaccurately treats the electron correlation which plays the most significant role in the estimation of the excited/ionized state energies. Since the number of electrons increases down the group as well as across the periodic table (for neutral species), the error in estimation of correlation energy through the second order MBPT increases and hence, the accuracy of calculated IP value decreases. However, we do not find any significant deviation in our computed CCLRT IP value (see Table I, fourth column), and this is exactly what we expect from CCLRT formalism. Since the CCLRT-IP method (also CCLRT-EA) is formally equivalent to the core-valence-extensive CC theory (an infinite order version of MBPT), it is expected that this method will correctly estimate the dynamical and nondynamical electron correlation effect and, thereby, will provide the correct description of the excited state of interest and its energy.

Table II presents the computed CCLRT shake-up state energies (also called satellite state energies) of Be and Mg atoms and compares with the experimental value (compiled

TABLE II. First ionization potential (in eV) of alkaline-earth metals.

Atom	Configuration of the ionized state	Koopmans' IP	MBPT(2)	CCLRT	Experiment [a]
Be	$1s^2 2s (93\%)$	8.417	8.982	9.319	9.322
	$1s^2 4s (46\%)$			20.934	20.260
	$1s^2 5s (41\%)$				
	$1s^2 3s (10\%)$				
	$1s^2 3s (62\%)$			24.371	23.637
	$1s^2 5s (32\%)$				
	$1s^2 4s (50\%)$			25.852	25.109
	$1s^2 3s (28\%)$				
	$1s^2 5s (19\%)$				
	$1s 2s^2 (70\%)$	128.808	124.979	124.552	
	$1s 2s 6s (13\%)$				
Mg	$1s^2 2s^2 2p^6 3s (91\%)$	6.898	7.521	7.648	7.645
	$1s^2 2s^2 2p^6 3s 5s (53\%)$			16.924	16.300
	$1s^2 2s^2 2p^6 3s 6s (27\%)$				
	$1s^2 2s^2 2p^6 3s 4s (15\%)$				
	$1s^2 2s^2 2p^6 3s 4s (72\%)$			19.817	19.150
	$1s^2 2s^2 2p^6 3s 6s (27\%)$				
	$1s^2 2s^2 2p^6 3s 5s (43\%)$			21.284	20.440
	$1s^2 2s^2 2p^6 3s 6s (42\%)$				
	$1s^2 2s^2 2p^6 3s 4s (13\%)$				
	$1s^2 2s^2 2p^6 3s^2 (21\%)$	102.890	97.940	99.549	
	$1s^2 2s^2 2p_{1/2} 2p_{3/2}^4 3s^2 (75\%)$	62.267	57.998	59.551	
	$1s^2 2s^2 2p_{1/2}^2 2p_{3/2}^3 3s^2 (67\%)$	61.955	56.948	58.533	

[a]Reference [33].

TABLE III. Excitation energies (in cm^{-1}) of alkali metals.

Atom	Transition	MBPT(2)	CCLRT	Experiment [a]
Li	$2s_{1/2} \rightarrow 3s_{1/2}$	27188	27223	27206
	$2s_{1/2} \rightarrow 2p_{1/2}$	14915	14955	14903
	$2s_{1/2} \rightarrow 2p_{3/2}$	14916	14964	14904
Na	$2s_{1/2} \rightarrow 3s_{1/2}$	25544	25782	25739
	$2s_{1/2} \rightarrow 3p_{1/2}$	16783	16900	16956
	$2s_{1/2} \rightarrow 3p_{3/2}$	16801	16849	16973

[a]Reference [36].

from the excited state energies of the ionized species). Compared to the valence ionization potentials, the shake-up state energies are less accurate and are slightly overestimated. Nevertheless, the satellite state energies are still in good agreement with the experiment. These small but non-negligible discrepancies in the computation of satellite state energies can be explained as follows: Unlike the valence ionized states, the character of the shake-up states and its energy strongly depends upon the quality of the occupied as well as the virtual orbitals (to which an electron is being promoted). Therefore, we expect the use of extended basis functions might improve the quality of the shake-up states and its energy.

We present the excitation energies of Li and Na computed through CCLRT in Table III and compare with experiments and second order MBPT calculations with this present basis. Table III demonstrates that both the $s \rightarrow s$ and $s \rightarrow p$ transition energies are accurately estimated by the CCLRT method. Although the second order MBPT transition energies of lithium are more accurate than CCLRT, this agreement is most likely fortuitous, because the second order IP values are less accurate than the CCLRT. This conjecture is

also supported by the CCLRT transition energies of sodium which are more accurate and consistent than second order MBPT.

V. SUMMARY AND CONCLUDING REMARKS

In this article, we have developed and applied RCCLRT for computing ionization potentials. However, by properly defining the excitation operator $W_k^{\dagger}$, the CCLRT method in its present form can also be used to compute the energy difference of other types, viz., double-ionization potentials (DIPs), electron affinity, excitation energies, etc. As an illustrative numerical application, we have computed the ionization energies of Li, Be, Na, and Mg atoms and compared with the experiment. A uniform and excellent agreement with the experiment indicates the power of this theory. Though CCLRT is a core-extensive theory, the one-valence problem is a special case where CCLRT is formally equivalent to core-valence extensive multireference CC theory. Unlike MRCC, the energy difference calculation through CCLRT proceeds via the diagonalization of a nonsymmetric matrix, and, hence the convergence problem (which arises due to the presence of the intruder states) does not appear here. Unless an out of core diagonalization scheme is introduced, the CCLRT method may suffer from computational inefficiencies.

[1] J. Cizec, J. Chem. Phys. **45**, 4256 (1966); Adv. Chem. Phys. **14**, 35 (1969); J. Paldus, J. Cizec, and I. Shavitt, Phys. Rev. A **5**, 50 (1972); R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. **14**, 561 (1978).

[2] R. J. Bartlett, Annu. Rev. Phys. Chem. **359**, 32 (1981).

[3] R. Offerman, W. Ey, and H. Kümmel, Nucl. Phys. A **273**, 349 (1976); W. Ey, *ibid.* **296**, 189 (1978).

[4] I. Lindgren, Int. J. Quantum Chem., Symp. **12**, 33 (1978); Phys. Rev. A **31**, 1273 (1985).

[5] D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Mol. Phys. **33**, 955 (1977); A. Haque and D. Mukerjee, J. Chem. Phys. **80**, 5058 (1984); D. Mukherjee and S. Pal, Adv. Quantum Chem. **20**, 291 (1989), and references therein.

[6] D. Mukherjee, Chem. Phys. Lett. **125**, 207 (1986); Int. J. Quantum Chem., Symp. **20**, 409 (1986).

[7] S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, Chem. Phys. Lett. **137**, 273 (1987); J. Chem. Phys. **88**, 4357 (1988).

[8] I. Lindgren and D. Mukherjee, Phys. Scr. **93**, 151 (1987).

[9] W. Kutzelnigg, J. Chem. Phys. **77**, 3081 (1982); W. Kutzelnigg and S. Koch, *ibid.* **79**, 4351 (1983).

[10] W. Kutzelnigg, S. Koch, and D. Mukherjee, J. Chem. Phys. **87**,

5902 (1987); D. Mukherjee, W. Kutzelnigg, and S. Koch, *ibid.* **87**, 5911 (1987).

[11] B. Jeziorski and H. J. Monkhorst, Phys. Rev. A **24**, 1668 (1981).

[12] A. Haque and U. Kaldor, Chem. Phys. Lett. **117**, 347 (1985); **128**, 45 (1986); U. Kaldor, J. Chem. Phys. **87**, 467 (1987); Int. J. Quantum Chem., Symp. **20**, 445 (1986).

[13] S. R. Gwaltney and R. J. Bartlett, J. Chem. Phys. **108**, 6790 (1998).

[14] G. E. Brown and D. G. Ravenhall, Proc. R. Soc. London, Ser. A **251**, 105 (1951).

[15] S. A. Blundell, J. Sapirstein, and W. R. Johnson, Phys. Rev. D **45**, 1602 (1991).

[16] F. A. Parpia, J. Phys. B **31**, 1409 (1998), and references therein.

[17] M. Pernpointer, P. Schwerdtfeger, and B. A. Hess, J. Chem. Phys. **108**, 6739 (1998), and references therein.

[18] E. Eliav, U. Kaldor, Y. Ishikawa, M. Seth, and P. Pyykkö, Phys. Rev. A **53**, 3926 (1996); E. Eliav, U. Kaldor, Y. Ishikawa, and P. Pyykkö, Phys. Rev. Lett. **77**, 5350 (1996).

[19] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996).

[20] J. Sapirstein and W. R. Johnson, J. Phys. B **29**, 5213 (1996); S. A. Blundell, J. Sapirstein, and W. R. Johnson, Phys. Rev. D **45**, 1602 (1992).

[21] H. J. Monkhorst, Int. J. Quantum Chem., Symp. **11**, 421 (1977); E. Dalgaard and H. J. Monkhorst, Phys. Rev. A **28**, 1217 (1983).

[22] D. Mukherjee and P. K. Mukherjee, Chem. Phys. **39**, 325 (1979).

[23] S. Ghosh, D. Mukherjee, and S. N. Bhattarchyya, Chem. Phys. **72**, 1611 (1982); B. Kundu and D. Mukherjee, Chem. Phys. Lett. **179**, 468 (1991); B. Dutta, P. Sen, and D. Mukherjee, J. Phys. Chem. **99**, 6441 (1995).

[24] S. Ghosh, D. Mukherjee, and S. N. Bhattarchyya, Mol. Phys. **43**, 173 (1981); S. Roy, S. Sengupta, D. Mukherjee, and P. K. Mukherjee, Int. J. Quantum Chem. **29**, 205 (1986); S. Mukhopadhyay, D. Sinha, M. D. Prasad, and D. Mukherjee, Chem. Phys. Lett. **117**, 437 (1985).

[25] D. Sinha, S. K. Mukhopadyay, M. D. Prasad, and D. Mukherjee, Chem. Phys. Lett. **125**, 213 (1986); D. Mukhopadhyay, S. K. Mukhopadhyay, R. Chaudhuri, and D. Mukherjee, *ibid.* **154**, 544 (1989).

[26] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem., Symp. **18**, 255 (1984); J. Greetsen, M. Rittby, and R. J. Bartlett, Chem. Phys. Lett. **164**, 57 (1989).

[27] H. Koch, H. J. A. Jensen, P. Jorgensen, and T. Helgaker, J. Chem. Phys. **93**, 3345 (1990); H. Koch and P. Jorgensen, *ibid.* **93**, 3333 (1990).

[28] R. K. Chaudhuri, P. K. Panda, and B. P. Das, Phys. Rev. A **59**, 1187 (1999).

[29] I. P. Grant and H. M. Quiney, Adv. At. Mol. Phys. **23**, 37 (1988).

[30] D. Mukhopadhyay, S. Mukhopadhyay, R. Chaudhuri, and D. Mukherjee, Theor. Chim. Acta **80**, 441 (1991).

[31] H. Nakatsuji, Chem. Phys. Lett. **59**, 362 (1978); **67**, 329 (1979); H. Nakatsuji and K. Hirao, J. Chem. Phys. **68**, 2053 (1978); **68**, 4279 (1978); H. Nakatsuji, Int. J. Quantum Chem., Symp. **17**, 241 (1983).

[32] T. Koopmans, Physica (Amsterdam) **1**, 104 (1933).

[33] C. E. Moore, *Atomic Energy Level*, Natl. Bur. Stand. Ref. Data Ser. (U.S. GPO, Washington, DC, 1971).

[34] K. G. Dyall, I. P. Grant, and S. Wilson, J. Phys. B **17**, 493 (1984); **17**, 1201 (1984).

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

[36] W. L. Weise, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities*, Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 22 (U.S. GPO, Washington, DC, 1966), Vol. 2.