

Hybrid approach to relativistic Gaussian basis functions: Theory and applications

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We present a hybrid method to solve the relativistic Hartree-Fock-Roothan equations where the one- and two-electron radial integrals are evaluated numerically by defining the basis functions on a grid. This procedure reduces the computational costs in the evaluation of two-electron radial integrals. The orbitals generated by this method are employed to compute the ionization potentials, excitation energies, and oscillator strengths of alkali-metal atoms and elements of group IIIA through second-order many-body perturbation theory. The computed properties are in excellent agreement with the experiment and other correlated theories.

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I. INTRODUCTION

The two most critical choices in the application of many-body perturbation theory (MBPT) [1–3] (relativistic as well as nonrelativistic) to atomic and molecular systems involve the appropriate selection of basis functions and the partitioning of the full Hamiltonian H into a zeroth-order Hamiltonian H_0 and a perturbation V [4–6]. These choices become extremely important when highly accurate estimates of various properties are demanded from low-order perturbative computations. Intensive research has focused on developing appropriate basis sets and methods [5–8] to minimize the error between the theoretically computed properties and its experimental value. The strong dependence of the convergence of MBPT on the choice of H_0 was first demonstrated by Kelly [4] in his pioneering work on the beryllium atom. Using a V^{N-1} instead of the traditional V^N potential for the excited orbitals, Kelly obtained a vast improvement in the perturbative convergence for that atom. He also demonstrated that more rapid convergence can be achieved from a shifted denominator that corresponds to the summation of a certain class of diagrams to all order.

It is well known that a theoretical treatment of heavy atoms must incorporate certain special features that are not essential for light atoms. This is largely due to the fact that the relativistic effects are so large for heavy atoms that it is imperative to treat them by using the relativistic Dirac equation. Despite its enormous computational complexity and cost, tremendous progress has been made over the past decade and a half in solving the four-component Dirac equations for many-electron systems using numerical Dirac-Fock (DF) and the finite basis set expansion (FBSE) method [9–21]. The numerical atomic DF self-consistent-field calculation is more compact and accurate, but its extension to molecular systems (multicenter many-electron systems) is cumbersome. Moreover, the generation of a virtual orbital is tedious and frequently encounters convergence difficulties. The FBSE method, on the other hand, is rather simple, and

its extension to molecules is straightforward. Also, the generation of occupied and virtual orbitals do not require separate computations.

The success of the relativistic FBSE method lies in its proper imposition of kinetic-balance condition [22] between the large and small component spinor which in essence can be regarded as a proper boundary condition upon the basis set. Several papers by Grant and co-workers [13] and Parpia [23], among others, document the success of the relativistic FBSE method. However, in their finite basis set calculation for light to heavy atoms ($Z=2-50$ and 80), Grant and co-workers [13] employed kinetically balanced Slater-type orbitals (STO's) which have the correct functional behavior but are particularly unsuitable for analytical self-consistent-field (SCF) molecular calculations. Gaussian-type orbitals (GTO's) or contracted Gaussian-type orbitals (CGTO's), on the other hand, are suitable in the evaluation of multicenter integrals in molecules. It was shown by Ishikawa, Baretty, and Binning [24] that GTO's can give rise to a natural description of the relativistic wave functions within a finite nucleus.

The most important feature of the FBSE method in the STO [$\exp(-\zeta r)$] or GTO [$\exp(-\zeta r^2)$] framework is to determine the appropriate exponential parameter ζ , because the quality of the wave function largely depends upon this parameter, and in recent years there has been an increased interest in finding out the appropriate exponential parameter and contraction coefficients (for CGTO's) that can provide correct functional behavior of the relativistic wave-functions at the nucleus [15,25–28]. For instance, Matsuoka and co-workers [26] have reported accurate configuration average DF energies for various atoms through the FBSE method using a kinetically balanced well-tempered basis set in the framework of the finite nuclear size approximation. While Matsuoka and co-workers [26] used a well-tempered Gaussian basis set in computing DF energies, Clementi and Corongio [15] employed a kinetically balanced geometric-type exponent for the Gaussian primitives, and obtained DF energies for various atoms that are comparable to the numerical DF value [29]. Later Malli and Styszynski [28] reported all-electron *ab initio* fully relativistic DF and DF Breit calculations for polyatomic systems using a relativistic universal Gaussian basis set, and recently Pernpointer, Schwerdtfegen

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and Hess [27] employed a relativistic CGTO basis set in their relativistic coupled cluster calculation for the nuclear quadrupole moment of CsF. Though the Slater (STO) and Gaussian (GTO) types of basis functions are most widely used in atomic many-body calculations, this choice is, in principle, arbitrary. Since it is beyond the scope of this present work to discuss this aspect at length, we refer the review articles by Grant [30] and Sapirstein [31] for details.

We have developed a numerical procedure to solve the atomic relativistic DF-SCF equations using the FBSE method. This approach is basically a hybrid of numerical and analytical DF (FBSE) methods. Here, the large and small component radial functions are expanded in terms of Gaussian primitives on a grid using appropriate constraints on the small component radial basis to impose the kinetic-balance condition. While the large- and small-component parts of the radial functions are generated (on a grid) through the FBSE procedure, the one- and two-electron radial integrals are evaluated numerically to avoid the complicated analytical expressions for the two-electron direct and exchange radial integrals (the analytical evaluation of one-electron radial integral is rather straight forward). This is the part which differs from the conventional FBSE method for solving DF-SCF or Hartree-Fock-SCF equations. This procedure (numerical computation of two-electron integrals) also provides an easy way to reduce the $N(N+1)/2$ operations to N_c operations (N and N_c correspond to the number of basis set and occupied orbitals, respectively) in DF-SCF computation, and, thereby, reduces the computational time of relativistic self-consistent-field calculations for heavy atoms. In the perturbative computations of ground- and excited-state properties, the two-electron radial integrals are also directly computed (numerically) wherever they appear to avoid the two-electron integral storage problem. In this paper, we present some pilot calculations of the ionization potentials and excitation energies of alkali-metal and elements of group IIIA computed through second order MBPT using relativistic wave functions obtained from the hybrid DF-SCF approach.

In Sec. II, we describe the hybrid DF-SCF method that has been used to generate the relativistic single-particle atomic orbitals for post-Dirac-Fock computations. Section III briefly reviews the background of the MBPT approach for computing ionization potentials, electron affinities, and excitation energies. The numerical results are presented in Sec. IV and compared with other perturbative calculations, where available. We make some concluding remarks in Sec. V.

II. HYBRID RELATIVISTIC HARTREE-FOCK-ROOTHAN EQUATION

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

$$H = \sum_{i=1}^N [c \vec{\alpha}_i \cdot \vec{p}_i + (\beta_i - 1)mc^2 + V_{\text{nuc}}(r_i)] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad (2.1)$$

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

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad (2.2)$$

where $\vec{\sigma}$ stands for the 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

$$E = \langle \Phi | \sum_{i=1}^N [c \vec{\alpha}_i \cdot \vec{p}_i + (\beta_i - 1)mc^2 + V_{\text{nuc}}(r_i)] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} | \Phi \rangle, \quad (2.3)$$

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

$$u(r, \theta, \phi) = \begin{pmatrix} r^{-1} P_{n\kappa}(r) \chi_{\kappa m}(\theta, \phi) \\ i r^{-1} Q_{n\kappa}(r) \chi_{-\kappa m}(\theta, \phi) \end{pmatrix}, \quad (2.4)$$

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

$$\int_0^\infty dr [P_{n\kappa}(r) P_{n'\kappa}(r) + Q_{n\kappa}(r) Q_{n'\kappa}(r)] = \delta_{nn'}. \quad (2.5)$$

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

$$\kappa = -2(j-l)(j + \frac{1}{2}), \quad (2.6)$$

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 as

$$\chi_{\kappa m} = \sum_{\sigma = \pm 1/2} C(l \frac{1}{2} j; m - \sigma, \sigma) Y_{l, m - \sigma}(\theta, \phi) \eta_\sigma, \quad (2.7)$$

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 η_σ stands for the two-component spinors.

With these definitions, it can be easily shown that the application of the variation principle to Eq. (2.3) leads to a coupled integrodifferential equations in $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$. Therefore, to obtain the numerical wave functions, we have to solve these two coupled integrodifferential equations [32]. Alternatively, a pseudoeigenvalue equation (Hartree-Fock-Roothan) [33] can be obtained by using an analytic expansion-type wave function and minimizing the energy functionals E with respect to the expansion coefficients.

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-Roothan equation (the 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 basis 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 introduce a hybrid scheme 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-Roothan equations. Since the basis functions are defined on a grid and the matrix elements appearing in the relativistic Hartree-Fock-Roothan equations are evaluated numerically, this scheme can be regarded as a combination of numerical and analytical approaches 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.,

$$P_{n\kappa}(r) = \sum_p C_{\kappa p}^L g_{\kappa p}^L(r) \quad (2.8)$$

and

$$Q_{n\kappa}(r) = \sum_p C_{\kappa p}^S g_{\kappa p}^S(r), \quad (2.9)$$

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 GTO's that has the following form for the large component:

$$g_{\kappa p}^L(r) = \mathcal{N}_p^L r^{n_\kappa} e^{-\alpha_p r^2}, \quad (2.10)$$

with

$$\alpha_p = \alpha_0 \beta^{p-1}, \quad (2.11)$$

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

$$g_{\kappa p}^S(r) = \mathcal{N}_p^S \left(\frac{d}{dr} + \frac{\kappa}{r} \right) g_{\kappa p}^L(r), \quad (2.12)$$

where

$$\mathcal{N}_p^S = \sqrt{\frac{\alpha_p}{2n_\kappa - 1} [4(\kappa^2 + \kappa + n_\kappa) - 1]}. \quad (2.13)$$

Using the above definitions, the Dirac-Fock-Roothan equation for a closed-shell system can be cast into a pseudoeigenvalue equation of the form

$$FC = SC\epsilon, \quad (2.14)$$

where F is the Fock matrix, and S , C , and ϵ are overlap, eigenvector, and eigenvalue matrices, respectively. This pseudoeigenvalue equation is first transformed into an eigenvalue equation $F'C' = C'\epsilon$, which on diagonalization produces the desired eigenvalues (ϵ) and eigenvectors ($C = S^{-1/2}C'$). Since the detailed derivation of the relativistic Hartree-Fock-Roothan equation and its matrix elements (analytical as well as numerical form) has been discussed in detail by several authors [9,13], we conclude this section by reiterating that the DF matrix elements appearing in the hybrid relativistic Hartree-Fock-Roothan equations are evaluated numerically to avoid the evaluation of a complicated analytical expression of two-electron matrix elements, and to improve the accuracy of the orbital properties. The present procedure also provides an easy route to implement N_c (N_c specifies the number of occupied orbitals) operations instead of N^2 (N denotes the number of basis functions) for the evaluation of the two-electron radial integrals that appear in the DF-SCF equation. A brief outline of the scheme is the following.

In the SCF procedure, the integrals and 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

$$\psi_i = \sum_{\mu=1}^N C_{\mu i} \phi_\mu, \quad (2.15)$$

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

$$\begin{aligned} U_{ij} &= \sum_c \langle \phi_i \psi_c | \frac{1}{r_{12}} | \phi_j \psi_c \rangle \\ &\equiv \sum_c \sum_\mu \sum_\nu C_{\mu c}^* C_{\nu c} \langle \phi_i \phi_\mu | \frac{1}{r_{12}} | \phi_j \phi_\nu \rangle, \end{aligned} \quad (2.16)$$

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 a $\{\phi, \psi\}$ basis. This is trivial, because the occupied orbitals can be updated (like density matrix) during the SCF iteration 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 two two-index transformation.

III. THEORY

A. Overview of multireference MBPT method

Multireference many-body perturbation theory (MBPT) may be regarded as a reformulation of the exact Schrödinger equation into a small reference space that is a subspace of the full Hilbert space. This reduction is achieved by first separating the atomic or molecular orbitals into three sets—the core $\{c\}$, valence $\{v\}$, and excited orbitals $\{e\}$ —and then introducing projection operators P for the reference space (also called valence or model space) and Q for its orthogonal complement or virtual space:

$$P = \sum_{i=1}^d |\alpha\rangle\langle\alpha| \quad (3.1)$$

and

$$Q = 1 - P = \sum_{m=d+1}^{\infty} |m\rangle\langle m|, \quad (3.2)$$

where the sets $\{\alpha\}$ and $\{m\}$ are, respectively, reference and complementary space functions, and d is the dimensionality of the reference space. With the aid of these two projectors, the exact N -electron time-independent Schrödinger equation can be transformed into the equation

$$H_{\text{eff}}|\Psi_{\lambda}^0\rangle = E|\Psi_{\lambda}^0\rangle \quad (3.3)$$

involving the effective Hamiltonian H_{eff} ,

$$H_{\text{eff}} = PHP + PHQ(E - QHQ)^{-1}QHP, \quad (3.4)$$

where H is the exact Hamiltonian, and H_{eff} acts only on the reference space spanned by $\{\alpha\}$ and produces the exact eigenvalues E for the selected states as given by the full-space Schrödinger equation.

Certain approximations are necessary to solve Eq. (3.4), since the right-hand side involves the unknown eigenvalue E and Q space states, which, in principle are of infinite dimension. The expansion of the denominator about the zeroth-order eigenvalue transforms the Brillouin-Wigner type H_{eff} [Eq. (3.4)] to the Rayleigh-Schrödinger-type effective Hamiltonian (H_{eff})

$$H_{\text{eff}} = PHP + PHQ(E_0 - H_0)^{-1}QHP + \dots \quad (3.5)$$

The exact Hamiltonian H is partitioned into H_0 (the zeroth-order Hamiltonian) and V (the perturbation), where the zeroth-order Hamiltonian is taken to be diagonal in P and Q subspaces, and may be written as a sum of diagonal one-electron operators h_0 defined by

$$h_0 = \sum_i \epsilon_i |i\rangle\langle i|, \quad (3.6)$$

where i runs over all orbitals, and ϵ_i is the i th orbital energy. The partitioning of the orbitals must ensure a well-defined separation of the orbital energies between core, valence, and excited orbitals. Failure to meet this requirement introduces numerical instabilities into the perturbative computations. Although, in the above, we have chosen the zeroth-order energy to be the ‘‘sum over orbitals,’’ this choice is, *in principle*, at our disposal, and *in practice* it strongly affects the convergence properties of the perturbative expansions. There are two general categories known as the generalized Möller-Plesset (MP) [34] and the generalized Epstein-Nesbet (EN) partitioning schemes [35]. The generalized MP partitioning utilizes a ‘‘sum over orbitals’’ treatment, whereas the generalized EN pursues a ‘‘sum over states’’ formulation in constructing the zeroth-order Hamiltonian H_0 . Different potentials may also be invoked to construct H_0 , and a wide range of potentials have been chosen [4,5] with varying degrees of success. The Hartree-Fock potential is the most widely used potential for MBPT computations, because many terms au-

tomatically vanish for this particular choice. The present second-order MBPT computation employs MP partitioning, where the zeroth-order energy is constructed from the Hartree-Fock potential.

B. Relativistic many-body perturbation theory

The relativistic Dirac-Coulomb Hamiltonian (presented in Sec. II) for a many-electron system may also be partitioned into $H = H_0 + V$, where

$$H_0 = \sum_{i=1}^N [c\vec{\alpha}_i \cdot \vec{p}_i + (\beta_i - 1)mc^2] - \sum_{i=1}^N \frac{Z(r_i)e}{r_i} + \sum_{i=1}^N U(r_i) \quad (3.7)$$

which subsequently redefines the perturbation V ,

$$V = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i=1}^N U(r_i), \quad (3.8)$$

where the single-particle operator $U(r_i)$ is introduced to account the effective (or average) potential experienced by an electron due to the presence of other electrons, and is known as the Hartree-Fock potential. The Schrödinger equation of the zeroth-order Hamiltonian H_0 provides a set of orbitals that are first partitioned into core, valence, and excited orbitals and then two projectors P and Q are introduced to cast the N -electron Schrödinger equation into an effective Hamiltonian equation [Eq. (3.5)]. Finally, the effective Hamiltonian matrix is diagonalized to obtain the desired positive and negative eigenvalues. [Note that while carrying out relativistic MBPT calculations, negative energy states are excluded from sum over intermediate states ($|m\rangle$) to avoid *continuum dissolution*.]

The theoretical ionization process is usually described as $M \rightarrow M^+ + e$. However, the ionization process may also be represented as $M^+ + e \rightarrow M$. That is to say, the ionization potential (IP) can be computed either by estimating the energy required to remove an electron from the neutral atomic or molecular system or evaluating the energy released during the electron attachment (EA) process to its positively charged counterpart. Though in principle the computed energies will be the same, in practice the theoretical treatment of these two processes are not equally convenient. For alkali-metal atoms or systems with one electron in the outermost shell, it is convenient to estimate the ionization potential by computing the energy released due to the addition of an electron to its positively charged species (a closed-shell core). It is to be emphasized that although, theoretically, the above two processes should provide identical numbers, for a truncated many-body calculation they need not be the same, because the orbitals and their corresponding energies are not identical in these two situations. In the first case the core and virtual orbitals experience the potential due to the valence electron (singly occupied orbital), but this potential is not present in the second case.

The second quantized representation of electron attachment process to a closed-shell core is

$$|\Psi_{\lambda}^0\rangle = a_v^{\dagger} |\Phi_0\rangle = a_v^{\dagger} (\prod_{c=1}^N a_c^{\dagger}) |0\rangle. \quad (3.9)$$

Here $|0\rangle$ and $|\Phi_0\rangle$ represent the true and closed-shell vacuum states, respectively. Operators a_v^\dagger and a_c^\dagger denote the valence and core creation operators, respectively. For a Na-like system, the core orbitals are $1s_{1/2}, 2s_{1/2}, 2p_{1/2}$, and $2p_{3/2}$, and the valence orbitals will be $3s_{1/2}, 3p_{1/2}$, and $3p_{3/2}$. For convenience, we introduce the notation $\alpha, \beta, \gamma, \dots$ for core orbitals, p, q, r, \dots for excited orbitals, u, v, w, \dots for valence orbitals, and m and n for valence and/or excited orbitals.

The second quantized representation of the zeroth-order Hamiltonian H_0 and the perturbation V are

$$H_0 = \sum_{i,j} h_{ij} a_i^\dagger a_j + U_{ij} a_i^\dagger a_j \quad (3.10)$$

and

$$V = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k - U_{ij} a_i^\dagger a_j, \quad (3.11)$$

where

$$h_{ij} = \int d^3r \psi_i(\vec{r})^\dagger \left[c \vec{\alpha}_i \cdot \vec{p}_i + (\beta_i - 1) m c^2 - \frac{Z(r_i) e}{r_i} \right] \psi_j(\vec{r}), \quad (3.12)$$

$$U_{ij} = \int d^3r \psi_i(\vec{r})^\dagger U(\vec{r}) \psi_j(\vec{r}), \quad (3.13)$$

and

$$g_{ijkl} = e^2 \int \int \frac{d^3r_1 d^3r_2}{|\vec{r}_1 - \vec{r}_2|} \psi_i(\vec{r}_1)^\dagger \psi_j(\vec{r}_2)^\dagger \psi_k(\vec{r}_1) \psi_l(\vec{r}_2). \quad (3.14)$$

Using these definitions, the second-order effective Hamiltonian matrix [Eq. (3.5)] for electron attachment (EA) and detachment (IP) processes can be expressed in terms of single particle orbital (for the Hartree-Fock potential) as

$$EA^{(2)} = \epsilon_v + \sum_{\alpha, m, n} \frac{g_{\alpha v m n} \bar{g}_{m n \alpha v}}{\epsilon_v + \epsilon_\alpha - \epsilon_m - \epsilon_n} - \sum_{\alpha, \beta, m} \frac{g_{\alpha \beta v m} \bar{g}_{v m \alpha \beta}}{\epsilon_\alpha + \epsilon_\beta - \epsilon_v - \epsilon_m} \quad (3.15)$$

and

$$IP^{(2)} = -\epsilon_\alpha - \sum_{\beta, \gamma, p} \frac{g_{\beta \gamma \alpha p} \bar{g}_{\alpha p \beta \gamma}}{\epsilon_\beta + \epsilon_\gamma - \epsilon_\alpha - \epsilon_p} + \sum_{\beta, p, q} \frac{g_{\beta \alpha p q} \bar{g}_{p q \beta \alpha}}{\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q}, \quad (3.16)$$

where ϵ 's are the single-particle orbital energies, and \bar{g}_{ijkl} represents

$$\bar{g}_{ijkl} = g_{ijkl} - g_{ijlk}. \quad (3.17)$$

While the first term of Eqs. (3.15) and (3.16) accounts for the PHP of Eq. (3.5), the second and third terms of Eqs. (3.15) and (3.16) represents the second term of Eq. (3.5). The first terms of Eqs. (3.15) and (3.16) are generally called the

Koopmans' EA/IP value. The second and third terms of Eqs. (3.15) and (3.16) are the correlation and relaxation contribution to the second order EA/IP, respectively.

The problems of continuum dissolution first occurs at second order because of the appearance of the energy denominator. Unless the restriction of the summation over only positive energy states is in place, this could lead to a vanishing energy denominator.

IV. RESULTS

A. Ionization potentials of neutral alkali-metal atoms and group-III A elements

We present the ionization potentials of alkali-metal atoms computed through second-order MBPT in Table I, and compare with experiments [36] and with the second-order perturbative calculations of Johnson and co-workers [19]. The only difference between these two theoretical calculations lie in the choice of basis functions (apart from the dimension of the basis function). While Johnson and co-workers generated the basis through the B -spline method, we employ geometric Gaussian function (with $\alpha_0 = 0.0052$ and $\beta = 2.75$) to construct the atomic orbital basis. The entire computation is performed with a basis that ranges from $20s15p15d15f$ (for lithium) to $28s24p20d16f10g$ (for francium).

Table I clearly demonstrates that the accuracy in the ionization potential estimated through Koopmans' theorem [37] of alkali-metal atoms decreases with increasing atomic number. For instance, the Koopman ionization potential for the $s_{1/2}$ state starts off with an accuracy of 1% for $2s_{1/2}$ state of lithium, and finally ends up with 12% for the $7s_{1/2}$ state of francium. We also observe similar trends for $p_{1/2}$ and $p_{3/2}$ states, where separation between $p_{1/2}$ and $p_{3/2}$ states increases (degenerate in lithium) with increasing atomic number.

Apart from sodium, inclusion of the second-order MBPT terms (relaxation and correlation contribution) significantly improves the agreement with the experiment, especially for the heavy alkali metals. While the accuracy of our computed ionization potential for lighter atoms is similar to that of Johnson and co-workers [19], the accuracy in the estimated IP for heavy atoms (cesium and francium) is better than theirs. In particular, our computed IP values for cesium are comparable to the CCSD (coupled cluster calculation with singles and doubles) of Eliav *et al.* [20]. This small but non-negligible difference in computed IP for cesium and francium between our results and that of Johnson *et al.* clearly is a basis set effect. However, it should be noted that while pursuing higher-order MBPT calculations, the use of such a large basis will be highly computer intensive unless some deep-lying core and high-lying virtual orbitals are discarded from the calculations.

Table II compares the ionization potentials of group-III A elements computed through second-order MBPT with the experiments [36]. We found several interesting features for this series. First of all, unlike the alkali-metal atoms, the Koopmans' IP values do not change appreciably down the series. Second, the second-order MBPT provides a less accurate IP value for these elements compared to the alkali-metal atoms. The deviation in computed IP values for these elements is quite expected because the nondynamical correlation effects

TABLE I. Second-order ionization potential (in a.u.) of alkali-metal atoms.

Atom	Ionizing orbital	KT	Δ^c	This work		Others ^a	Experiment ^b
				Second order	Abs. error (%)		
Li	$2s_{1/2}$	0.19631	0.00162	0.19793	0.11	0.19797	0.19814
	$2p_{1/2}$	0.12862	0.00134	0.12996	0.22	0.13001	0.13024
	$2p_{3/2}$	0.12862	0.00134	0.12996	0.22	0.13001	0.13024
	$3s_{1/2}$	0.07370	0.00034	0.07404	0.18	0.07415	0.07418
Na	$3s_{1/2}$	0.18204	0.00558	0.18762	0.65	0.18790	0.18886
	$3p_{1/2}$	0.10947	0.00168	0.11115	0.40	0.11123	0.11160
	$3p_{3/2}$	0.10939	0.00167	0.11106	0.41	0.11119	0.11152
	$4s_{1/2}$	0.07003	0.00120	0.07123	0.49	0.07141	0.07158
K	$4s_{1/2}$	0.14751	0.01181	0.15932	0.13	0.15994	0.15952
	$4p_{1/2}$	0.09568	0.00436	0.10004	0.31	0.10033	0.10035
	$4p_{3/2}$	0.09547	0.00430	0.09977	0.11	0.10005	0.10009
	$5s_{1/2}$	0.06095	0.00268	0.06363	0.13	0.06395	0.06371
Rb	$5s_{1/2}$	0.13939	0.01393	0.15333	0.12	0.15430	0.15351
	$5p_{1/2}$	0.09078	0.00497	0.09575	0.48	0.09626	0.09619
	$5p_{3/2}$	0.08995	0.00474	0.09469	0.44	0.09518	0.09511
	$6s_{1/2}$	0.05861	0.00315	0.06176	0.00	0.06216	0.06177
Cs	$6s_{1/2}$	0.12753	0.01519	0.14272	0.27	0.14511	0.14310
	$6p_{1/2}$	0.08556	0.00642	0.09198	0.15	0.09253	0.09212
	$6p_{3/2}$	0.08374	0.00567	0.08941	0.23	0.08996	0.08962
	$7s_{1/2}$	0.05515	0.00341	0.05856	0.19	0.05939	0.05867
	$7p_{1/2}$	0.04177	0.00219	0.04396	0.001		0.04393
	$7p_{3/2}$	0.04106	0.00202	0.04308	0.001		0.04310
	$8s_{1/2}$	0.00419	0.00962	0.01381			
Fr	$7s_{1/2}$	0.13184	0.01926	0.15110	0.96	0.15271	0.14967
	$7p_{1/2}$	0.08584	0.00788	0.09327	0.69	0.09431	0.09392
	$7p_{3/2}$	0.08041	0.00542	0.08583	0.46	0.08656	0.08623
	$8s_{1/2}$	0.05605	0.00411	0.06016		0.06074	

^aReference [31].^bReference [36].^cCorrelation and relaxation contribution to the ionization potential.

are quite large for these elements due to the quasidegeneracy of the highest-lying occupied orbitals. For example, the $2s_{1/2}$, $2p_{1/2}$, and $2p_{3/2}$ orbitals of Boron are quasidegenerate and hence, a multireference MBPT treatment is absolutely necessary for this system to improve the accuracy and low-order perturbative convergence rate.

Generally, the theoretical treatment of the electron attachment process is difficult because the correlation and relaxation effects tend to cancel each other (see Fig. 1), and the success of the theoretical treatment depends upon the relative importance of these two effects. For alkali-metal atoms, the relaxation effect is small compared to the correlation effect (especially for heavy alkali metals) and, hence, they do not cancel each other. Figure 1 also illustrates that while the contribution from the relaxation part is small and roughly the same for all the alkali metals beyond sodium, the correlation contribution steadily increases with the increasing atomic number. This pattern, however, may change at higher-order MBPT and, in fact, has also been observed by Johnson and

co-workers [19]. It is also evident from Table I that correlation and relaxation effects are important for inner orbitals, which indicates that the contribution of correlation and relaxation term will be large for deep-lying core orbitals. The precise estimation of correlation and relaxation effects for the deep-lying (or inner) core, therefore, requires higher-order many-body effects and, hence, it is imperative that high-order perturbative computations (like the coupled cluster method) are necessary for the accurate estimation of core ionization.

B. Excitation energies of neutral alkali-metal atoms and elements of group IIIA

The direct computation of hole-particle excitation energy involves the matrix elements ($H_{\alpha p}^{\beta q}$), which through second-order MBPT can be written as

$$H_{\alpha p}^{\beta q} = \langle \Phi_{\beta}^q | H_{\text{eff}}^{(2)} | \Phi_{\alpha}^p \rangle = \langle \Phi_0 | a_{\beta}^{\dagger} a_q H_{\text{eff}}^{(2)} a_p^{\dagger} a_{\alpha} | \Phi_0 \rangle. \quad (4.1)$$

TABLE II. Second-order ionization potential (in a.u.) of group-III A elements.

Atom	Ionizing orbital	KT	Δ^b	This work		Experiment ^a
				Second order	Abs. error (%)	
B	$2p_{1/2}$	0.27587	0.02984	0.30571	0.25	0.30494
	$2p_{3/2}$	0.27579	0.02983	0.30562		
	$3s_{1/2}$	0.11451	0.00596	0.12047		
	$4s_{1/2}$	0.05172	0.00168	0.05340		
Al	$3p_{1/2}$	0.19522	0.02444	0.21966	0.15	0.21998
	$3p_{3/2}$	0.19472	0.02439	0.21911		
	$4s_{1/2}$	0.09709	0.00646	0.10355		
	$5s_{1/2}$	0.04563	0.00224	0.04787		
Ga	$4p_{1/2}$	0.19609	0.02569	0.22178	0.59	0.22046
	$4p_{3/2}$	0.19275	0.02576	0.21851		
	$5s_{1/2}$	0.09996	0.00697	0.10693		
	$6s_{1/2}$	0.04670	0.00231	0.04901		
In	$5p_{1/2}$	0.18881	0.02666	0.21541	1.30	0.21263
	$5p_{3/2}$	0.17974	0.02544	0.20518		
	$6s_{1/2}$	0.09383	0.00822	0.10205		
	$7s_{1/2}$	0.04422	0.00307	0.04729		
Tl	$6p_{1/2}$	0.19863	0.02397	0.22260	0.80	0.22446
	$6p_{3/2}$	0.16602	0.02300	0.18902		
	$7s_{1/2}$	0.09647	0.00789	0.10436		
	$8s_{1/2}$	0.04526	0.00279	0.04805		

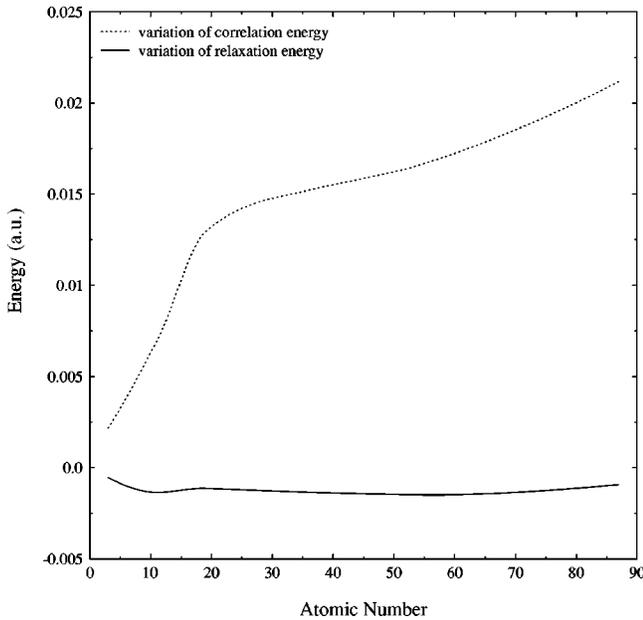
^aReference [36].^bCorrelation and relaxation contribution to the ionization potential.

FIG. 1. Variation of correlation (dotted line) and relaxation energy (solid line) as a function of atomic number for alkali-metal atoms.

Appropriate expansion of $H_{\text{eff}}^{(2)}$ yields

$$\begin{aligned}
 H_{\alpha p}^{\beta q} = & \left[\epsilon_p \delta_{pq} + \sum_{r,s,\gamma} \frac{g_{q\gamma rs} \bar{g}_{rsp\alpha}}{\epsilon_p + \epsilon_\gamma - \epsilon_r - \epsilon_s} \right. \\
 & \left. - \sum_{r,\gamma,\delta} \frac{g_{\gamma\delta pr} \bar{g}_{qr\gamma\delta}}{\epsilon_\delta + \epsilon_\gamma - \epsilon_r - \epsilon_q} \right] \delta_{\alpha\beta} \\
 & + \left[-\epsilon_\alpha \delta_{\alpha\beta} - \sum_{r,\gamma,\delta} \frac{g_{\gamma\delta\beta r} \bar{g}_{r\alpha\gamma\delta}}{\epsilon_\delta + \epsilon_\gamma - \epsilon_r - \epsilon_\alpha} \right. \\
 & \left. + \sum_{r,s,\gamma} \frac{g_{\alpha\gamma rs} \bar{g}_{rs\alpha\beta\gamma}}{\epsilon_\beta + \epsilon_\gamma - \epsilon_r - \epsilon_s} \right] \delta_{pq} + \bar{g}_{q\alpha\beta p} \\
 & + \sum_{r,\gamma} \frac{\bar{g}_{\alpha\gamma pr} \bar{g}_{qr\beta\gamma}}{\epsilon_\beta + \epsilon_\gamma - \epsilon_q - \epsilon_r} + \sum_{r,\gamma} \frac{\bar{g}_{q\gamma\beta r} \bar{g}_{r\alpha\gamma p}}{\epsilon_p + \epsilon_\gamma - \epsilon_r - \epsilon_\alpha}.
 \end{aligned} \tag{4.2}$$

Here the first two terms of the right-hand side of Eq. (4.2) corresponds to the matrix elements for electron attachment and detachment processes, and the next two terms corresponds to two-body effective interaction for excitation process. In Eq. (4.2) the last sum excludes $\gamma = \alpha$ and $p = r$.

TABLE III. Second-order excitation energies (in cm^{-1}) and oscillator strengths of alkali-metal atoms.

Atom	Transition	Energy	This work		Experiment ^a	
			Abs. error(%)	Osc. str.	Energy	Osc. str.
Li	$2s_{1/2} \rightarrow 2p_{1/2}$	14915	0.08	0.770	14903	0.753
	$2s_{1/2} \rightarrow 2p_{3/2}$	14916	0.08		14904	
	$2s_{1/2} \rightarrow 3s_{1/2}$	27188	0.07		27206	
Na	$3s_{1/2} \rightarrow 3p_{1/2}$	16783	1.00	1.041	16956	0.982
	$3s_{1/2} \rightarrow 3p_{3/2}$	16801	1.00		16973	
	$3s_{1/2} \rightarrow 4s_{1/2}$	25544	0.08		25739	
K	$4s_{1/2} \rightarrow 4p_{1/2}$	13010	0.19	1.231	12985	1.02
	$4s_{1/2} \rightarrow 4p_{3/2}$	13068	0.19		13043	
	$4s_{1/2} \rightarrow 5s_{1/2}$	21101	0.36		21026	
Rb	$5s_{1/2} \rightarrow 5p_{1/2}$	12636	0.45	1.338	12579	
	$5s_{1/2} \rightarrow 5p_{3/2}$	12868	0.40		12817	
	$5s_{1/2} \rightarrow 6s_{1/2}$	20097	0.18		20134	
Cs	$6s_{1/2} \rightarrow 6p_{1/2}$	11178	0.40	1.414	11134	
	$6s_{1/2} \rightarrow 6p_{3/2}$	11700	0.27		11732	
	$6s_{1/2} \rightarrow 7s_{1/2}$	18469	0.36		18535	
Fr	$7s_{1/2} \rightarrow 7p_{1/2}$	12692				
	$7s_{1/2} \rightarrow 7p_{3/2}$	14324				
	$7s_{1/2} \rightarrow 8s_{1/2}$	19957				

^aReference [38].

However, the computation of excitation energies for alkali-metal atoms involving the highest singly occupied (at the Dirac-Fock level orbital) is rather simple, because the effective two-body interactions do not appear. For example, the $2s_{1/2} \rightarrow 2p_{1/2}$ transition process for the lithium atom can be expressed as

$$\begin{aligned}
 |\Phi_{2p_{1/2}}\rangle &= |1s^2 2p_{1/2}\rangle = a_{2p_{1/2}}^\dagger a_{2s_{1/2}} |1s^2 2s\rangle \\
 &= a_{2p_{1/2}}^\dagger a_{2s_{1/2}} a_{2s_{1/2}}^\dagger |1s^2\rangle \equiv a_{2p_{1/2}}^\dagger |1s^2\rangle. \quad (4.3)
 \end{aligned}$$

Therefore, the $2s_{1/2} \rightarrow 2p_{1/2}$ transition energy through second order MBPT reduces to

$$\begin{aligned}
 \Delta E_{2s_{1/2} \rightarrow 2p_{1/2}} &= \langle \Phi_{2p_{1/2}} | H_{\text{eff}}^{(2)} | \Phi_{2p_{1/2}} \rangle - \langle \Phi_{2s_{1/2}} | H_{\text{eff}}^{(2)} | \Phi_{2s_{1/2}} \rangle \\
 &\equiv \langle 1s^2 | a_{2p_{1/2}} H_{\text{eff}}^{(2)} a_{2p_{1/2}}^\dagger | 1s^2 \rangle \\
 &\quad - \langle 1s^2 | a_{2s_{1/2}} H_{\text{eff}}^{(2)} a_{2s_{1/2}}^\dagger | 1s^2 \rangle. \quad (4.4)
 \end{aligned}$$

A careful analysis shows that the quantity on the right-hand side of Eq. (4.4) is nothing but the difference in the ionization potential value (in terms of the neutral lithium atom) or the difference in the electron affinity value (in terms of the positively charged lithium atom). Therefore, once the valence ionization potentials are known for these alkali-metal atoms, the excitation energies involving the highest singly occupied orbital (at the Dirac-Fock level) can be easily evaluated by computing the difference in the ionization potential value.

Excitation energies and oscillator strengths computed through second-order MBPT (using second-order energy and an unperturbed dipole matrix element) for alkali-metal atoms and group-III A elements are compared with the experiment [38] in Tables III and IV. These tables demonstrate that the second-order MBPT estimates the $s_{1/2} \rightarrow p_{1/2}$ transition energies more accurately than $s_{1/2} \rightarrow p_{3/2}$ for alkali-metal atoms. Here we also find that the error in the estimation of $s_{1/2} \rightarrow s_{1/2}$ transition energies is less (on an average) compared to $s_{1/2} \rightarrow p_{1/2}$ and $s_{1/2} \rightarrow p_{3/2}$ for alkali-metal atoms. While the second-order single-reference MBPT provides an accurate estimate for the excited states of alkali-metal atoms, it yields somewhat inaccurate (compared to alkali-metal atoms) excited-state energies for the group-III A elements. This deviation in the estimation of the excitation energies for elements of group III A is not unexpected, since the highest occupied s and p orbitals are fairly close lying for these elements, configurations like $ns^2 np (J = \frac{1}{2})$ and $np^3 (J = \frac{1}{2})$ interact strongly with each other [39]. Therefore, these two configuration state functions (CSF's) should be included in the reference space for an accurate description of the ground and excited states. In other words, a multireference MBPT treatment is necessary for an accurate description of the ground and excited states for these elements. Since our second-order single reference space MBPT for the ground- and excited-state energy computations do not treat the CSF np^3 as reference space states, these CSF's act as intruder states [40], and, thereby, affect the perturbative convergence. An extensive study of this problem is underway.

TABLE IV. Second-order excitation energies (in cm^{-1}) of group-III A elements.

Atom	Transition	This work	Abs. error(%)	Others ^a	Experiment ^b
B	$2p_{1/2} \rightarrow 3s_{1/2}$	40656	1.54		40040
	$2p_{3/2} \rightarrow 3s_{1/2}$	40635	1.53		40024
	$3s_{1/2} \rightarrow 4s_{1/2}$	14720	1.66		14969
Al	$3p_{1/2} \rightarrow 4s_{1/2}$	25483	0.51		25347
	$3p_{3/2} \rightarrow 4s_{1/2}$	25362	0.51		25234
	$4s_{1/2} \rightarrow 5s_{1/2}$	12220	0.99		12342
Ga	$4p_{1/2} \rightarrow 5s_{1/2}$	25207	1.69		24789
	$4p_{3/2} \rightarrow 5s_{1/2}$	24489	2.20		23962
	$5s_{1/2} \rightarrow 6s_{1/2}$	12712	0.66		12796
In	$5p_{1/2} \rightarrow 6s_{1/2}$	24880	2.08		24373
	$5p_{3/2} \rightarrow 6s_{1/2}$	22634	2.14		22160
	$6s_{1/2} \rightarrow 7s_{1/2}$	12018	0.75		11929
Tl	$6p_{1/2} \rightarrow 7s_{1/2}$	25951	1.99	27048	26478
	$6p_{3/2} \rightarrow 7s_{1/2}$	18581	0.56	19196	18685
	$7s_{1/2} \rightarrow 8s_{1/2}$	12359	0.70		12268

^aReference [41].^bReference [38].

V. CONCLUSION

We have presented valence ionization potentials, excitation energies, and oscillator strengths of alkali-metal atoms and group-III A elements computed through single-reference second-order MBPT, where the single-particle orbitals are generated by solving the Dirac-Fock Hamiltonian in a finite Gaussian basis. Since the present procedure computes the one- and two-electron radial integrals numerically by defining the atomic orbitals on a grid, it is easy to implement the $\approx N_c$ dependence (N_c is the number of occupied orbitals) for the number of operations needed to evaluate the two-electron integrals that appears in the Dirac-Fock self-consistent field equation. The numerical accuracy achieved for single-valence-electron atoms promises that this hybrid method will be accurate for other many-electron atomic systems and,

with some modifications, can also be applied to molecular systems.

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