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Citation: [The Journal of Chemical Physics](#) **95**, 395 (1991); doi: 10.1063/1.461441

View online: <http://dx.doi.org/10.1063/1.461441>

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Ab initio correlated valence shell effective Hamiltonian method for atomic and molecular systems

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(Received 31 December 1990; accepted 25 March 1991)

A new method for correlated electronic structure calculations that makes explicit reference to *valence* electrons only is presented for atomic and molecular processes in which the core electrons remain inert. The method is based on constructing a valence Hamiltonian that includes a one-electron effective potential for the core–valence interactions. It *exactly* reproduces *all* properties (wave functions, energies, etc.) of an all electron calculation with frozen core wave functions with same bases. It has no adjustable parameters, and no restrictions on the choice of basis sets. It yields considerable savings of computer time and space over the corresponding all electron calculations. Self-consistent field (SCF) and complete active space multiconfiguration self-consistent field (CAS-MCSCF) test calculations on ground states of F , F^- , and S are presented.

I. INTRODUCTION

Recent advances in our ability to perform accurate atomic and molecular electronic structure calculations is impressive^{1,2} and yet currently restricted to approximately 40 electron systems beyond which the computational expense becomes prohibitive. The majority of chemically interesting processes often involve the dynamics of larger number of electrons. Among them, a large class involves atoms and molecules in which the core electrons undergo negligible change, hence changes of the properties of such systems are determined mainly by the dynamics of valence electrons—their correlation effect, their polarization, and their interaction with core electrons. High-energy processes involving core excitations, for example, would not fall into this category. In pictorial terms, the core electrons, which are more strongly bound to the nuclei and shielded from the environment by valence electrons, remain largely *inert*. On the other hand, the valence electrons, being more weakly bound, are the first to come into contact with the environment. Thus their dynamics largely determine the properties of the system. Formation of a molecule is a classic example of such a process. The idea is that if an effective potential can be constructed to replace the effect of the dynamics of atomic core electrons, one can exclusively focus on the dynamics of valence electrons to determine the properties. Methods based on this idea are categorized as frozen core potential calculations.^{3–18}

For such systems we assume that it is possible to partition a system of N -electrons into $2m$ inner core electrons and n valence electrons, where, $2m + n = N$. We assume that the core electrons form a doubly occupied closed shell configuration which is totally symmetric. We assume that the process does not involve core excitations. We assume further that the scope of this development lies within the basis set expansion representation of the Hamiltonian.

The method proposed in this paper requires no parameters for the description of the core potential. The atomic core potential is treated exactly, within the limits of a finite

basis set expansion, assuming that the core electrons are represented by a closed shell wave function. This method can be applied to any choice of the valence basis.

II. BACKGROUND AND FROZEN CORE EFFECTIVE POTENTIAL

We start by defining the formalism required to perform a correlated calculation for the solutions of the Schrödinger equation for an N -electron system using an effective potential for the core electrons. Let $|0\rangle$ define a core for $2m$ electrons in which all m orbitals are doubly occupied (singlet coupled). These orbitals by definition remain passive. Let Ψ be the wave function for the system, which can be written in its most general form,

$$\Psi = \sum_{k=1}^M \Phi_k C_k, \quad \Phi_k = \Omega_k^+ |0\rangle, \quad (1)$$

where the M configurations $\{\Phi_k\}$ are written as the action of an operator which adds n valence electrons to $|0\rangle$ in different orbitals, so that Ω_k^+ contains only valence operators (in normal order). For example, to describe the ground state of $NH(b^1\Sigma^+)$ it may be reasonable to take $|0\rangle \equiv (1\sigma^2 2\sigma^2)$ and the remaining four valence electrons may be occupied by the addition of four orbitals by $\{\Omega_k^+\}$ from the set $\{3\sigma, 4\sigma, \dots, 1\pi, 2\pi, \dots\}$. These core orbitals are designated by Greek subscripts α, β, \dots , and the orbitals not occupied in $|0\rangle$ by Roman subscripts p, q, r, s, \dots . The subscripts i, j, k, l denote unrestricted orbitals. The Ψ satisfies the Schrödinger equation (SE)

$$H\Psi = E\Psi. \quad (2)$$

In this description, it can be shown^{4,5} that the matrix elements

$$\langle \Phi_k | H | \Phi_l \rangle = \langle \underline{\Phi}_k | \underline{H} | \underline{\Phi}_l \rangle, \quad (3)$$

where $\underline{\Phi}_k$ is the same as Φ_k , except the core orbitals have been deleted. Thus all $\underline{\Phi}_k$ are n -valence electron configurations and \underline{H} in second quantized form is

$$\begin{aligned} \underline{H} &= \langle 0 | H | 0 \rangle + \sum_{ij} \langle i | F | j \rangle N [i^+ j] \\ &+ \frac{1}{2} \sum_{ijkl} \langle ij | kl \rangle N [i^+ j^+ lk], \end{aligned} \quad (4)$$

where

$$\begin{aligned} F_{ij} &\equiv \langle i | F | j \rangle = \langle i | h | j \rangle + \sum_{\alpha} (2 \langle i \alpha | j \alpha \rangle - \langle i \alpha | \alpha j \rangle), \\ &\equiv \langle i | h | j \rangle + \langle i | 2J^c - K^c | j \rangle \\ &\equiv \langle i | h | j \rangle + \langle i | U | j \rangle. \end{aligned} \quad (5)$$

Here, $\langle i | h | j \rangle (\equiv \langle \phi_i | h | \phi_j \rangle)$ and $\langle ij | kl \rangle (\equiv \langle \phi_i(1) \phi_j(2) | 1/r_{12} | \phi_k(1) \phi_l(2) \rangle)$ are the usual one- and two-electron integrals. The summation indices i, j, k, l now span the outer (valence + unoccupied) orbitals only. The second term is the matrix representation of the core potential over the valence orbitals, i.e., the core–valence interaction potential containing the coulomb and the exchange (nonlocal) terms. The core energy is

$$\begin{aligned} E_c &\equiv \langle 0 | H | 0 \rangle \\ &= 2 \sum_{\alpha} \langle \alpha | h | \alpha \rangle + \sum_{\alpha\beta} \{ 2 \langle \alpha\beta | \alpha\beta \rangle - \langle \alpha\beta | \beta\alpha \rangle \}. \end{aligned} \quad (6)$$

These results of Eqs. (3–5) are proven in the Appendix. The main point to be noted is that the total energy of an all electron (AE) wave function of Eq. (1) may be subdivided into four separate parts:⁶ (i) An intracore energy, a sum over isolated atomic cores, $\sum_A E_c^A$; (ii) an interaction energy between cores (molecular cases) $E_c(AB)$; (iii) a core–valence interaction energy U ; (iv) an intravalence energy.

The first part corresponds to isolated atoms, and is a constant (negative). It is entirely absent for the valence energy, which energy is the sum of the last three parts. The second part involves core–core coulomb and exchange repulsion terms, pertinent only for molecular cases; it is internuclear geometry dependent and contains coulomb and exchange interactions between cores and is dealt with in Sec. III C. Incidentally, the first two parts are contained in the core energy expression of Eq. (6). The core–valence interactions are grouped together into a one particle potential F of Eq. (5). The F need be calculated only once at the beginning of the calculations. The use of this potential then obviates any further reference to core orbitals in the construction of the matrix elements of H . This is helpful since it reduces the size of the lists of two-electron integrals and density matrix elements which need to be accessed. Within the assumption of the construction of Ψ in Eq. (1), this development is exact. Thus the valence orbitals would be identical to those of the AE calculation, including their nodal structure. The only restriction on the core and the outer orbitals is that together they form an *orthonormal* set. This is the well-known all electron frozen core approximation (AEFCA).^{5,7,8}

In this paper our intention is to attain this AEFCA result *exactly* by *separately* performing *first*, a calculation for the core potential, and *second*, use this potential to perform a calculation for the valence electrons *only*. For molecular cases, only the second step is performed at each internuclear geometry. The basic idea is to rearrange the AEFCA formalism in a manner so as to maximize separation of those parts of the interactions (core–core and core–valence) which can

be performed on *isolated* centers and stored. Using this information, in the second (separate) step the valence energy of n electrons is calculated. Our aim is to reproduce *correlated* AEFCA calculations for atoms and molecules.

The calculation suggested using the valence Hamiltonian of Eq. (4) is still laborious because the two-electron integrals over the *entire* orbital basis (core + valence) must be calculated at all geometries of the molecule, since, to maintain the orthogonality to the core, the valence orbitals are linear combinations over the entire basis set. However, since the construction of the effective core potential and its use for the description of the dynamics of valence electrons is performed in two separate steps using bases appropriate for each step, any attempts to impose orthonormality among the core and valence orbitals results in three different problems: Let P and Q be the core and valence projection operators,

$$P = \sum_{\alpha} |\alpha\rangle \langle \alpha|, \quad Q = 1 - P. \quad (7)$$

One needs to evaluate the valence energy

$$E = \langle \Psi | Q H Q | \Psi \rangle. \quad (8)$$

(i) Application of projection operators to the wave function $Q\Psi$ and consequently to orbitals requires that the one- and two-electron integrals over the entire set of basis functions be calculated and transformed appropriate to the irreducible representation of the system.

(ii) Alternatively, if the projection operator is applied to the Hamiltonian, QHQ , there results an infinite series expression^{7,8,9} which can no longer be truncated to sums of only one- and two-electron operators as in Eq. (4). Indeed, such a procedure introduces complex many-body operators. For example, the projections carried out through unitary operators $\exp(iS)$, leads to^{5,9}

$$\begin{aligned} e^{-iS} H e^{iS} &= H - i[S, H] + (-i)^2/2! [S, [S, H]] \\ &+ (-i)^3/3! [S, [S, [S, H]]] + \dots \end{aligned} \quad (9)$$

(iii) The SE [Eq. (2)] can be rewritten as a nonlocal effective potential, called the generalized Philips–Kleinman potential:¹⁰

$$(H + U)\Psi = E\Psi, \quad \text{with } U = -HP - PH + PHP + EP. \quad (10)$$

Here, since the nonlocal potential U involves the unknown energy E , an iterative solution must be performed. The degree of difficulty encountered in all of the above calculations is similar to that of the frozen core approximation. Of course, the literature contains a variety of approximations to these procedures which apply mainly to SCF wave functions for the valence electrons for which case these procedures become equivalent.^{3,11}

Finally, relinquishing the orthogonality constraint produces valence orbitals that collapse into the core region.¹² Thus the description of the distributions of the valence electrons and the ensuing calculated properties depart correspondingly from the AEFCA results that one intended to mimic.

In this paper, we shall construct an effective core potential (core–valence interactions) to be calculated only once irrespective of the geometry of the molecule and devise a

valence-electron-only method which uses this potential to calculate correlated wave functions and energies for ground and excited states such that it exactly reproduces the result of AEFCAs correlated calculations.

III. THEORETICAL DEVELOPMENT

There are two steps to the use of the method that we now describe. The first is to construct in a chosen basis the core potential U and the orbitals $\{\chi_\alpha\}$. The next step is to choose a valence basis set $\{\eta_i\}$, appropriate to the atomic or molecular system. From the set $\{\eta_i\}$ we construct another orthonormal set $\{\phi_k\}$ which is *also* orthogonal to the core orbitals. This latter construction is performed *solely* as linear combinations among the valence set. This avoids having to calculate and transform integrals over the entire (core + valence) basis. Once these two tasks are accomplished it is clear from the valence Hamiltonian of Eq. (4) that the set $\{H, \phi_k\}$ can be used for fixed $\{\chi_\alpha, U\}$ for any correlated calculation (MCSCF, CI, MBPT, CC, etc.). The method we present will be referred to as correlated valence shell effective Hamiltonian (CVSEH) method.

A. Construction of effective core potential (ECP)

In this section we construct the frozen-core effective potential U . We note that in Eq. (5) the orbital indices i, j refer to the atomic or molecular valence orbitals in which the calculations are being performed, whereas, the calculation of U is to be performed for a given atom in the chosen basis for the atom.

We propose that the one-electron operator $U \equiv 2J^c - K^c$ in Eq. (5) be simply represented as a matrix in a near complete *one-center* basis set,^{13,18} in particular the current atomic basis. The aim is to mimic the AEFCAs potential F , of Eq. (5) for valence orbitals $\{\phi_i\}$ constructed at a separate (second) step while avoiding calculations of *mixed* (core-valence) two-electron integrals $2\langle\phi_i|\chi_\alpha|\phi_j|\chi_\alpha\rangle - \langle\phi_i|\chi_\alpha|\chi_\alpha|\phi_j\rangle$ appearing in Eq. (5) in that step. For the atomic basis $\{g_p\}$, (e.g., a nonorthogonal set of Gaussian functions), on a center, with $\sigma_{pr} = \langle g_p|g_r\rangle$, the representation of the orbital ϕ_i has the form,

$$\phi_i = \sum_{pr} \langle\phi_i|g_p\rangle (\sigma^{-1})_{pr} \langle g_r|. \quad (11)$$

Then substituting Eq. (11), the matrix element of U in Eq. (5) becomes

$$\langle\phi_i|U|\phi_j\rangle = \sum_{p,q} \langle\phi_i|g_p\rangle \hat{U}_{pq} \langle g_q|\phi_j\rangle, \quad ij = 1, n, \quad (12)$$

where

$$\hat{U}_{pq} = \sum_r (\sigma^{-1})_{pr} U_{rs} (\sigma^{-1})_{sq}, \quad U_{rs} = \langle g_r|U|g_s\rangle. \quad (13)$$

For orthonormal bases, $\sigma_{pq} = \delta_{pq}$, then, $\hat{U}_{pq} = \langle g_p|U|g_q\rangle$. A very useful simplification results if the set $\{g_i\}$ is taken to be the orthonormal set consisting of the core orbitals $\{\chi_\alpha\}$ plus outer (valence + unoccupied) orbitals $\{\chi_p\}$ obtained from the SCF calculations of the core (in the first step), $\{g_i\} \equiv \{\chi_\alpha, \chi_p\}$, and if the valence orbitals (in the second step) $\{\phi_i\}$ are constructed to be orthogonal to $\{\chi_\alpha\}$, $\langle\phi_i|\chi_\alpha\rangle = 0$ (see Sec. III B). Then, Eqs. (12) and (13) become

$$\langle\phi_i|U|\phi_j\rangle = \sum_{p,q}^{m'} \langle\phi_i|\chi_p\rangle \hat{U}_{pq} \langle\chi_q|\phi_j\rangle, \quad \hat{U}_{pq} = \langle\chi_p|U|\chi_q\rangle. \quad (14)$$

Alternatively, the matrix representation of the core potential U in this basis is

$$U = \sum_{p,q}^{m'} \chi_p \rangle \hat{U}_{pq} \langle\chi_q|, \quad \hat{U}_{pq} = \langle\chi_p|U|\chi_q\rangle, \quad ij = 1, n. \quad (15)$$

Note, that here χ_p and χ_q refer only to the *outer* orbitals of the center and $m' < m$. Thus from a valence orbital basis $\{\phi_i\}$ the AEFCAs potential F of Eq. (5) can be *exactly* constructed from the $\{\hat{U}_{pq}, \langle\phi_i|\chi_p\rangle\}$. One can calculate and store over the outer atomic orbitals $\{\chi_p\}$ the matrix \hat{U}_{pq} according to Eq. (14). The claim is that it is more efficient to calculate the mixed integral $\langle\phi_i|U|\phi_j\rangle$ through mixed overlaps $\langle\phi_i|\chi_p\rangle$ than explicitly as two-electron integrals as in Eq. (5). We use the same procedure to calculate mixed core-outer-core two-electron integrals as mixed overlaps in Sec. II C, in terms of the same matrix $\{\hat{U}_{pq}\}$. The computational efficiency of this procedure is discussed in Sec. V. The completeness of the $\{\chi_\alpha, \chi_p\}$ basis (containing diffuse, and polarization functions) must also hold for a molecular Hamiltonian because the one-center expansion Eq. (11) must still hold. Even for large m' , a symmetric storage of $m'(m' + 1)/2$ elements can be easily handled for a given atom. This avoids the fitting of the local and/or the nonlocal parts of U by some analytical potential¹⁴⁻¹⁶ and the ensuing errors in such a representation. Operationally, for the molecular cases, while the set $\{\chi_p, \hat{U}_{pq}\}$ corresponds to each of the atomic centers A , the set $\{\phi_i\}$ corresponds to molecular valence orbitals. This also implies that a molecular valence basis should not be constructed as a union of such atomic sets since each one of them is intended to be complete and thus the union would result in linear dependencies.

B. Construction of valence orbitals orthogonal to core

The aim here is to show that given two sets of bases $\{\chi_j, j = 1, m\}$ and $\{\eta_i, i = 1, n\}$, $n > m$, which span two subspaces of an inner product space V with nonzero intersections $S_{ji} = \langle\chi_j|\eta_i\rangle \neq 0$ for some j and i , it is possible to obtain *at least* $n - m$ orbitals ϕ_k constructed *solely* as linear combinations among $\{\eta_i\}$, which are orthogonal to all χ_j and have *no* components of $\{\chi_j\}$. Furthermore, there are at most m orthogonal orbitals $\{\psi_l\}$ which have components of $\{\chi_j\}$. That is

$$\phi_k = \sum_i C_{ki} \eta_i, \quad \text{such that } \langle\chi_j|\phi_k\rangle = 0 \quad (16a)$$

and

$$\psi_l = \sum_i C_{li} \eta_i + \sum_i D_{li} \chi_i, \quad \text{such that } \langle\chi_j|\psi_l\rangle = 0, \quad (16b)$$

for all allowed values of j, k , and l . The coefficients C_{ki}, D_{li} are constants. For our applications, the set $\{\chi_j\}$ represents the core orbitals (linear combinations among core basis functions) and the $\{\eta_i\}$ the valence basis functions. We shall also use the notation, $\boldsymbol{\eta} = (\eta_1, \dots, \eta_n)^+$ and $\boldsymbol{\chi} = (\chi_1, \dots, \chi_m)^+$ to represent column vector of orbitals.

We now describe a procedure, which by construction, accounts for linear dependencies among the core projections

sian dot product, $e_i e_j = \delta_{ij}$. Then the A matrix, its row echelon form \tilde{A} , and Γ , are

$$A = \begin{bmatrix} -0.40816, & 0.81632 \\ -0.04081, & 0.08163 \\ -0.08163, & 0.16326 \\ -0.04081, & 0.08163 \end{bmatrix},$$

$$\tilde{A} = \begin{bmatrix} -0.40816, & 0.81632 \\ 0.00000, & 0.00000 \\ 0.00000, & 0.00000 \\ 0.00000, & 0.00000 \end{bmatrix},$$

$$\Gamma = \begin{bmatrix} 1 & 0 & 0 & 0 \\ -0.1 & 1 & 0 & 0 \\ -0.2 & 0 & 1 & 0 \\ -0.1 & 0 & 0 & 1 \end{bmatrix}. \quad (25)$$

Thus the row dimension of the A matrix is $p = 1$, i.e., of the two core orbitals, projected onto the valence space, only one is linearly independent. Thus $3(=4-1)$ valence orbitals can be constructed solely as linear combinations among $\{\eta_1, \eta_2, \eta_3, \eta_4\}$ which are orthogonal to the core orbitals χ_1 and χ_2 having no component of χ_1 and χ_2 , according to Eq. (23). These are

$$\begin{aligned} \phi_1 &= -0.1\eta_1 + \eta_2, & \phi_2 &= -0.2\eta_1 + \eta_3 \\ \text{and} & & & \\ \phi_3 &= -0.1\eta_1 + \eta_4. \end{aligned} \quad (26)$$

For completeness, the fourth orthogonal orbital $\psi_1 = \eta_1 - 0.40816\chi_1 + 0.81632\chi_2$, contains χ_1 and χ_2 . Thus calculations for valence electrons can be performed in the orthogonal space of ϕ_1, ϕ_2 , and ϕ_3 .

Thus at most one primitive Gaussian in the valence basis for each core orbital ensures orthogonalization. For iterative optimizations such as the MCSCF (or SCF), in the second step, orthogonality of the valence orbitals to the core still holds since these involve unitary transformations among the valence orbitals which by construction are initially orthogonal to the core.

We now summarize the steps for the construction of core potential and their subsequent use for correlated calculations for the valence electrons only.

(i) For an atom, perform an SCF calculation using the large basis and recognize the core and the valence electrons and the corresponding orbitals that they occupy.

(ii) Calculate \tilde{U}_{pq} from Eq. (14) for each center A , and store $m'(m'+1)/2$ elements, m' is the number of outer functions of center A .

To perform correlated calculations for atoms, we follow these steps:

(iii) Choose a valence basis $\{\eta_i\}$ and orthogonalize them to the core to yield $\{\phi_i\}$ as described in Sec. II B.

(iv) Transform $\tilde{U}_{pq} \rightarrow U_{ij}$ over the valence orbital basis according to Eq. (14).

(v) Construct a new one-electron Hamiltonian F as in Eq. (5).

(vi) Solve the Schrödinger equation with the Hamiltonian of Eq. (4) for the valence electrons only within the approximation desired.

(vii) Add the core energy from Eq. (6), to the valence electronic energy obtained in step (vi).

C. Molecular case

To treat molecular cases, the implication of the form of the valence Hamiltonian in Eq. (4) is that U , the molecular effective core-valence potential, is a superposition of each of the atomic core potentials U^A ,

$$\langle \phi_i | U | \phi_j \rangle = \langle \phi_i | \sum_A U^A | \phi_j \rangle, \quad (27)$$

where, U^A is given by Eq. (15),

$$U^A = \sum_{p,q}^{m'(A)} |\chi_{p(A)}\rangle \langle U^A \rangle_{pq} \langle \chi_{q(A)}|, \quad (28)$$

$$(U^A)_{pq} = \langle \chi_{p(A)} | U^A | \chi_{q(A)} \rangle.$$

The AEFCA core energy E_c of Eq. (6) for an orthonormal set of core orbitals, holds without change for atomic cases. For molecular cases the core energy of Eq. (6) is over molecular core orbitals and thus involves calculations of mixed (multicenter) integrals and overlaps over atomic core orbitals, which we now address. The core wave function consisting of closed shell (doubly occupied) Slater determinants constructed using the n_A, n_B, \dots , doubly occupied orbitals of A, B, \dots , is¹⁹

$$\Phi = a(\Phi_A \Phi_B \dots), \quad (29)$$

$$E_c = \langle \Phi | H | \Phi \rangle / \langle \Phi | \Phi \rangle$$

$$= \sum_{ij} h_{ij} \Delta_{ji} + \frac{1}{2} \sum_{ijkl} \langle ij | kl \rangle (\Delta_{ik} \Delta_{jl} - \Delta_{il} \Delta_{jk})$$

$$+ \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}, \quad (30)$$

where $\Delta = S^{-1}$ is the inverse of the overlap matrix between occupied orbitals. The one-electron operator h contains the kinetic energy and the electron-nuclear attraction terms on each center as well as the one-center-electron-other-nucleus attraction terms, for electron i of A

$$h = \sum_A h^A(i) + \sum_B \sum_{i \in A} h^{BA}(i), \quad h^{BA}(i) = \frac{Z_B}{r_{Bi}}. \quad (31)$$

The last term in Eq. (30) is the nuclear repulsion term between core A and B . The most difficult types of integrals in Eq. (30) are the four center integrals of the type $\langle \alpha\beta | \chi\delta \rangle$, where $\alpha \in A, \beta \in B, \chi \in C, \delta \in D$. We show now the calculation procedure using the one-center expansion, say on center A and basis $\{\alpha_i\}$,

$$\langle \alpha\beta | \chi\delta \rangle = \sum_{ijk} \langle \beta | \alpha_i \rangle \langle \chi | \alpha_j \rangle \langle \delta | \alpha_k \rangle \langle \alpha\alpha_i | \alpha_j \alpha_k \rangle. \quad (32)$$

Thus a three index array $\langle \alpha\alpha_i | \alpha_j \alpha_k \rangle$ needs to be stored during the calculations of each center (in the first step).

However, a very convenient simplification arises (which is recommended and is also consistent with the AEFCA) if the interatomic distances R_{AB} are large enough to give no significant overlap between the core orbitals ij belonging to different centers, i.e., $S_{ij} \simeq 0$. Then Eq. (30) becomes,

$$E_c = 2 \sum_i h_{ii} + \sum_{ij} \{2 \langle ij | ij \rangle - \langle ij | ji \rangle\} + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}. \quad (33)$$

In this sum, when both the core orbitals i and j belong to some center A , the terms contribute to the intracore energy

of the center E_c^A given by Eq. (6), while the remaining terms contribute to the interaction energy between cores E_{AB} for $\alpha \in A$,

$$E_c = \sum_A E_c^A + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} + E_{AB}, \quad (34)$$

where E_{AB} is

$$\begin{aligned} E_{AB} &= \sum_{A \neq B} 2 \sum_{\alpha \in A} \langle \alpha | h^B | \alpha \rangle \\ &+ \sum_{A < B} 2 \sum_{\alpha \in A, \beta \in B} \{2 \langle \alpha \beta | \alpha \beta \rangle - \langle \alpha \beta | \beta \alpha \rangle\} \\ &\equiv \sum_{A \neq B} 2 \sum_{\alpha \in A} \langle \alpha | h^B | \alpha \rangle + \sum_{A < B} 2 \sum_{\alpha \in A} \langle \alpha | U^B | \alpha \rangle. \end{aligned} \quad (35)$$

The $U^B \equiv U$ is the same core operator of Eqs. (5) and (14). Expanding the core orbitals $\{\alpha \in A\}$ over the orthonormal set consisting of the core orbitals $\{\beta_c\}$ plus outer (valence + unoccupied) orbitals $\{\beta_p\}$ obtained from the SCF calculations of the core (in the first step) of center B , $\{\beta_c, \beta_p\}$, and since the core orbitals $\{\alpha \in A\}$ are assumed to have no significant overlap with core orbitals of other centers, $\langle \alpha | \beta_c \rangle = 0$, then, the second term of Eq. (35) becomes,

$$\langle \alpha | U | \alpha \rangle = \sum_{p,q}^{m'} \langle \alpha | \beta_p \rangle \hat{U}_{pq} \langle \beta_q | \alpha \rangle, \quad \hat{U}_{pq} = \langle \beta_p | U | \beta_q \rangle. \quad (36)$$

A similar representation with U replaced by h^B in Eq. (36) exists. Thus one store $m'(m' + 1)/2$ terms $(h^B)_{pq}$ also similar to \hat{U}_{pq} at step 1, and in step 2 constructs the appropriate overlaps $\langle \alpha | \beta_p \rangle$ in Eq. (36) to calculate the terms of Eq. (35). Alternatively, $\langle \alpha | h^B | \alpha \rangle$ being a one-electron two-center integral can be calculated "on the fly" in the second step.

For completeness, the expression of Eq. (34), which we use, can be brought to a more commonly used form,^{8,20} by performing a multipole expansion of the terms of the electronic interaction energy E_{AB} of Eq. (35) and retaining only the leading terms. The approximations with $\alpha \in A, \beta \in B$, are: (i) the Coulomb integrals $\langle \alpha \beta | \alpha \beta \rangle \approx 1/R_{AB}$; (ii) the exchange integrals $\langle \alpha \beta | \beta \alpha \rangle \approx 0$; (iii) electron-other-nucleus terms $\langle \alpha | h^B | \alpha \rangle \approx Z_B/R_{AB}$, $\langle \beta | h^A | \beta \rangle \approx Z_A/R_{AB}$. With these approximations in E_{AB} , the core energy of Eq. (34) becomes

$$\begin{aligned} E_c &= \sum_A E_c^A + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} + 4 \frac{n_A}{2} \frac{n_B}{2} \frac{1}{R_{AB}} \\ &- 2 \frac{n_A}{2} \frac{Z_B}{R_{AB}} - 2 \frac{n_B}{2} \frac{Z_A}{R_{AB}} \\ &= \sum_A E_c^A + \sum_{A < B} \frac{(Z_A - n_A)(Z_B - n_B)}{R_{AB}}. \end{aligned} \quad (37)$$

This is the commonly used screened nucleus point-charge electrostatic approximation for the core energy. It is obvious that our expression for the core energy in Eq. (34)–(36) is a much more accurate and of desirable form and is exact whenever core-other-core orbital overlap is vanishes.

To perform correlated calculations for molecules [following steps (i) and (ii)] we use the following:

(iii) Choose a molecular valence basis $\{\eta_i\}$ and orthogonalize them to the core orbitals belonging to each center to give $\{\phi_i\}$ as in Sec. II.

(iv) Transform the integrals $\Sigma_A (\hat{U}^A)_{pq} \rightarrow U_{ij}$ over the valence orbital basis according to Eqs. (14) and (27), giving the core–valence interactions and over the core orbitals as in Eq. (36) to give $U_{\alpha\alpha'}$ part of the core–core interaction energy.

(v) Construct a new one-electron Hamiltonian F as in Eqs. (5) and (6).

(vi) Solve the Schrödinger equation with the Hamiltonian of Eq. (4) for the valence electrons within the approximation desired.

(vii) Add the core–core interaction energy from Eq. (34) to the valence electronic energy obtained in step (vi).

IV. COMPUTATIONAL CONSIDERATIONS

The first consideration is the choice of basis sets. Two different types of basis sets are needed for these calculations. The first is needed for the calculations of a given atom's core SCF orbitals and also its outer orbitals that provide a one-center spectral representation of the core–valence and core–core interaction operators discussed, respectively, in Secs. III A and C, Eqs. (14) and (30). To test the quality of the basis set, we use the representation of the unit operator.

$$\langle \phi | \phi \rangle = 1 \approx \sum_{vu} \langle \phi | \chi_v \rangle \langle \chi_v | \chi_u \rangle \langle \chi_u | \phi \rangle. \quad (38)$$

Here, $\{\chi_v\}$ are the outer orbitals on center A and B and the ϕ is either a valence orbital on center A or B or a core orbital on center B . A particular placement of center B relative to A simulates the molecular environment of internuclear separation $R(A - B)$ spanning the limits R_- and R_+ . It is important to check the accuracy of the representations at both limits. The lower limit is determined to be the smallest interatomic distance for which the core orbitals remain unperturbed. For example, R_- small enough, for which the core orbitals overlap significantly, must be excluded since it violates the assumptions of the AEFCA. Note that the assumption of small core–core overlap is also inherent in Eq. (14). At the higher limit R_+ the accuracy of the expansion is determined by the number of diffuse functions (and their angular dependence) contained in the outer orbital part of the basis.

The second basis set is needed for the valence-electron-only calculation of the second step. The consideration here is the inclusion of functions to describe properties of the valence electrons of the atomic or molecular system at hand. This involves the usual considerations leading to inclusion of diffuse and polarization functions. This choice should be made to have as small as possible overlap with the core orbitals, i.e., tight, corelike, function should not be included. As discussed in Sec. III B, at most one primitive Gaussian function for each independent projection of core orbitals onto the valence space is needed to ensure orthogonalization of the valence space to the core. In practice, we have found that the dimensionality of space of intersection of the core and valence basis p is always less than m . A judicious choice of valence basis function $\{\eta_j\}$ which are nearly orthogonal to $\{\chi_i\}$, $\langle \eta_j | \chi_i \rangle \approx 0$, implies that $p \approx 0$.

The next consideration is the evaluation of the matrix elements of the core–valence potential U over the valence orbitals given in Eq. (14). This evaluation is exactly equivalent to a one-electron integral transformation $C^+ UC$ and can be easily evaluated as N_v^2 operations with storage of N_v intermediate elements.

A. Applications

Results of some test calculations are presented for the ground states of atomic system F , F^- , and S at the SCF as well as CSMCSCF level. A characteristic of our method is that in all aspects of valence electron properties (orbitals, energies, etc.) are exactly identical to the AEFCA at all (SCF and correlated) levels of the calculations for the same basis sets. This criterion also allows one to debug large parts of the computer program (except for the core–core interactions). Presently, our computer programs submodules that perform orthogonalization of the valence orbitals to the core of Sec. III B and the module that constructs core potential of Sec. III A are separate. We are in the process of automating and streamlining these computer codes into one more efficient unit. We shall in following publications present a more systematic set of results for molecular systems (i.e., including core–valence and core–core interactions of different centers of Sec. III C). The Columbus (ANL system of programs) was used to perform AEFCA calculations. Our valence–electron-only computer codes are modified versions of these codes.

For $F(2P)$ atom, $F^-(1S)$ ion, and $S(3P)$ the AEFCA calculations were performed using the core basis functions to be contracted Gaussian functions obtained from Huzinaga *et al.*²⁰ The SCF and CAS-MCSCF energies are given in

TABLE I. Comparison of AEFCA and valence-electron-only CVSEH method. All energies in atomic units.

Basis	Method	AEFCA energy (Hartrees)	CVSEH energies (Hartrees)	
			Valence energy	Total energy

<i>F</i> : core 1s ² ; core energy = − 75.445 124 Hartree				
	SCF ^a	− 99.407 206	− 23.962 082	− 99.407 206
	MCSCF ^{ab}	− 99.534 087	− 24.088 963	− 99.534 087
	SCF ^c		− 23.962 084	− 99.407 208
	MCSCF ^{cb}		− 24.088 974	− 99.534 098
<i>F</i> [−] : core 1s ² ; core energy = − 75.465 816 Hartree				
	SCF ^a	− 99.452 104	− 23.986 288	− 99.452 104
	MCSCF ^{ab}	− 99.625 681	− 24.159 865	− 99.625 681
	SCF ^c		− 23.986 292	− 99.452 108
	MCSCF ^{cb}		− 24.159 882	− 99.625 698
<i>S</i> : core 1s ² 2s ² 2p ⁶ ; core energy = − 386.936 253 Hartree				
	SCF ^d	− 397.504 597	− 10.568 344	− 397.504 597
	MCSCF ^{bd}	− 397.598 706	− 10.662 453	− 397.598 706
	SCF ^e		− 10.568 392	− 397.504 645
	MCSCF ^{be}		− 10.663 169	− 397.599 422

^a Basis containing 61 primitive Gaussian functions. CVSEH calculations with valence orbitals obtained from AEFCA results.

^b CAS-MCSCF with 12 active orbitals.

^c Valence basis containing 48 primitive Gaussian functions.

^d Basis containing 119 primitive Gaussian functions. CVSEH calculations with valence orbitals obtained from AEFCA results.

^e Valence basis containing 64 primitive Gaussian functions.

Table I. The first test we performed is to choose for the valence basis the special case of the valence orbitals obtained from the AEFCA calculations. This valence basis being orthogonal to the core $p = 0$, i.e., no transformation or reduction is required and this valence basis is exactly identical to the one in AEFCA calculations. The results given in the first two rows for each atom in Table I and the CVSEH and AEFCA results are identical. For the next set of calculations we constructed the valence bases for F , F^- , and S , respectively, from the original AE bases minus those that obviously (with large exponents) mainly contributed to the core orbitals and augmented the bases by one diffuse d -basis function with exponent 0.210 for F and F^- and 0.748 for S . The augmentation of the bases also makes the point that a separate valence-electron-only calculation (on a finite machine which thus puts a limit on the total number of basis functions) can always be performed with larger accuracy than the corresponding AEFCA calculation. These results are shown in the third and fourth rows of each atom in Table I.

V. SUMMARY, DISCUSSION, AND CONCLUSIONS

We have presented in this paper a new method for performing valence-electron-only calculations using the core–valence interaction as the effective potential to reproduce exactly the AEFCA results. The necessity of such a method arose because AEFCA calculations include basis functions ($N_c + N_v = N$) to describe the dynamics of the core and valence electrons simultaneously and involves the calculation of $2 - e$ integrals and their transformation over the entire orbital basis. These procedures require of the order of N^4 and N^5 arithmetic operations, respectively. In comparison, the CVSEH calculation would require approximately N_v^4 and N_v^5 operations, respectively, for integral evaluation and transformation, plus the calculations of $N_v N_c$ overlap matrix elements involving $N_v N_c^2$ operations and construction of core–valence potential matrix elements over the outer orbitals requiring $N_v N_c^2$ and N_c^3 operations for the core–core matrix over the outer orbitals. Thus the totals are

operations for AEFCA:

$$N^4 + N^5,$$

operations for CVSEH:

$$N_v^4 + N_v^5 + N_v N_c^2 + N_v N_c^2 + N_c^3 \leq N_v^4 + N_v^5 + 3N_v^3.$$

To set an upper bound for CVSEH operations, we have replaced N_c by N_v . Thus there is significant savings [at least of the order $N_v^5(r^5 - 1)$ operations, where the ratio $r > 1$, is $r = N/N_v$] to be obtained through CVSEH calculations over the AEFCA calculations. We have not included into these considerations SCF calculations for the core orbitals and core–valence interaction potentials U , since they are performed once only.

We have introduced a new procedure to orthonormalize the valence basis to the core orbitals by performing linear combinations among the valence functions only. This procedure has completely eliminated explicit (and almost always approximate) usage of many-electron projection operators so prevalent in the literature. Adoption of this procedure which itself is very inexpensive (row-echelon reduction is an

N_v^3 process) has not only produced a very clean formalism, it has allowed considerable computational efficiencies.

This method can be routinely used for correlated (MCSCF, CI, MBPT, CC) calculations for valence electrons of atoms and molecules.

We are presently trying to extend this procedure for the calculation of the interaction energy between N - and M -electron systems without restrictions implied by the frozen core. Thus the method can become useful, for example, for the calculation of intermolecular interactions.

ACKNOWLEDGMENTS

I am very grateful to Dr. Kent Richman for many valuable suggestions, and help with format and comparative assessment of other methods during the course of the development of this paper and Noah Adams for his help in performing initial literature search and discussions regarding orthogonalization procedure. Dr. Ron Shepard for valuable computational help regarding the ANL programs, Dr. Maciek Gutowski, Dr. Randy Shirts, and Dr. Tom Pickett for many discussions about this manuscript. We thank Ms. Tammy Capo-Banerjee for proofreading this manuscript. At Idaho National Laboratory, the work was supported by the U.S. Department of Energy under Contract No. DE-AC07-76ID01570.

APPENDIX

To show this, we shall write the Hamiltonian in the normal-order form

$$H = \sum_{ij} \langle i|h|j \rangle i^+ j + \frac{1}{2} \sum_{ijkl} \langle ij|kl \rangle i^+ j^+ lk.$$

Rewriting the one electron part I using Wick's theorem, we have,

$$\begin{aligned} I &= \sum_{ij} \langle i|h|j \rangle \{N(i^+ j) + N(i^+ j)\} \\ &= \sum_{\alpha} \langle \alpha|h|\alpha \rangle + \sum_{ij} \langle i|h|j \rangle N(i^+ j), \end{aligned}$$

since

$$N(i^+ j) = i^+ j = \langle 0|i^+ j|0 \rangle = \delta_{i\alpha} \delta_{j\alpha}.$$

Similarly, the two-electron part of the Hamiltonian can be rearranged using Wick's theorem as

$$\begin{aligned} II &= \frac{1}{2} \sum_{\alpha\beta} \{ \langle \alpha\beta|\alpha\beta \rangle - \langle \alpha\beta|\beta\alpha \rangle \} \\ &+ \sum_{ij\alpha} \{ \langle i\alpha|j\alpha \rangle - \langle i\alpha|\alpha j \rangle \} N(i^+ j) \\ &+ \frac{1}{2} \sum_{ijkl} \langle ij|kl \rangle N(i^+ j^+ lk). \end{aligned}$$

The Hamiltonian of the total system, can be rewritten as

$$\begin{aligned} H &= \langle 0|H|0 \rangle + \sum_{ij} \langle i|f|j \rangle N[i^+ j] \\ &+ \frac{1}{2} \sum_{ijkl} \langle ij|kl \rangle N[i^+ j^+ lk]. \end{aligned}$$

So far the orbital indices span over the total basis set, including the core orbitals. However, a representative matrix elements of Eq. (3) has the form,

$$\langle \Phi_{\alpha\beta\gamma\dots} | H' | \Phi \rangle \sim \langle 0 | \Omega' T H' T \Omega^+ | 0 \rangle,$$

where Ω and $(\Omega')^+$ create Φ and $\Phi_{\alpha\beta\gamma\dots}$, respectively, when operating on $|0\rangle$. In this expression all operators appear in normal order and only H can have core creation and annihilation operators in the order $\beta\alpha^+$. Since $\alpha^+ |0\rangle = 0$, any occurrence in the Hamiltonian of the core operators in this order $\beta\alpha^+$ will give zero matrix element. The calculation of the total energy $E = \langle \Phi | H' | \Phi \rangle$ of course, needs to be updated by the core-core interaction $\langle 0 | H | 0 \rangle$.

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