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Replacing the SCF Part in Hartree–Fock–SCF Method with Algebraic Geometry Optimization for One-Determinant Approximation of Molecular Ground and Excited States

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Abstract: The self-consistent field (SCF) part of the Hartree–Fock self-consistent field (HF-SCF) method is responsible for finding the ground state as the global minimum of the one-determinant approximation of the electronic energy, which is a fourth-order multivariable polynomial of the LCAO coefficients and Lagrange multipliers. In this work, we replace this SCF part with algebraic geometry along with the multivariable Newton slope method, which allows us to find not only the ground but also the lowest-lying excited states. Calculations on some molecular systems with different multiplicities are provided for demonstration. The relation of our algorithm to the Kohn-Sham density functional theory (KS-DFT) algorithm is also discussed along with the correlation energy, as well as the opportunity to calculate (e.g., characteristic X-ray radiations, Auger electrons, laser- and hyper-excitations). For easier reading, some details are collected in the Appendix.

Keywords: Hartree–Fock method, self-consistent field optimization, algebraic geometry, Buchberger's algorithm, multivariable Newton slope method, one-determinant approximation for ground and excited electronic states; ortho and para helium

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1. Introduction

For the ground state, the emblematic Hartree–Fock (HF) method solves the non-relativistic electronic Schrödinger equation for an N-electron molecular system (containing M atoms with Z_A nuclear charges at nuclear positions $\mathbf{R}_A$). It does so by approximating the ground state antisymmetric wave function with a single Slater determinant ($\Psi_0 \approx S_0$) and minimizing the energy functional $\langle S_0|H_{el}S_0\rangle$ with the constraint that keeps the molecular orbitals (MOs) orthonormal in S_0 providing the norm $\langle S_0|S_0\rangle = 1$. This energy minimization is performed mostly with the emblematic self-consistent field (SCF) method, which is well documented in textbooks (we use the standard notations) [1-3]. The total electronic energy for the ground state is $E_{0,tot} = E_{0,el} + V_{nn}$, wherein V_{nn} is the nuclear-nuclear repulsion term. For an even number of electrons (N) along with all molecule orbitals are doubly occupied (closed shell), the electronic energy approximation [1] is (see App.1 for excited states as well)

$$E_{0,el} \approx E_{0,el}(HF) \equiv \langle S_0|H_{el}S_0\rangle = 2\sum_{i=1}^{N/2}\langle i(1)|h|i(1)\rangle + \sum_{i=1}^{N/2}\sum_{j=1}^{N/2}(2\langle i(1)^2|r_{12}^{-1}|j(2)^2\rangle - \langle i(1)j(1)|r_{12}^{-1}|i(2)j(2)\rangle) \quad (1)$$

The shorthand notation, 1 for $\mathbf{r}_1$ and 2 for $\mathbf{r}_2$, was used. For open shells where at least one singly occupied MO (the N can be even or odd) is present, the energy functional $\langle S_0|H_{el}S_0\rangle$ is algebraically analogous to Eq.1; in algebraic view, only the integer factors differ. Importantly, it is always a linear combination of the molecular integrals. The linear combinations of atomic orbitals (LCAO) approximation for the i^{th} MO is

$$i(1) = \sum_{k=1\ldots K} c_{ik}G_k(1) \quad (2)$$

The set $\{c_{ik}\}$ in Eq.2 is called the LCAO coefficients for the basis set $\{G_k\}_{k=1,\ldots K}$. To avoid singular solutions, $K \geq N/2$ is set, and Gaussian basis set is used for analytical evaluations of the molecular integrals. The set $\{c_{ik}\}$ can be arranged as a rectangular matrix. Expanding Eq.1 by using Eq.2 yields a fourth-order multivariable polynomial of $\{c_{11},\ldots, c_{1K},\ldots, c_{N/2,1},\ldots, c_{N/2,K}\}$, i.e., the number of variables is a KN/2 dimension row vector. To minimize Eq.1 while keeping the N/2 MOs orthonormal, the Lagrangian on HF level, L(HF), is

$$L(HF) = \langle S_0|H_{el}S_0\rangle + \sum_{i=1}^{N/2}\sum_{j\geq i}^{N/2}\lambda_{ij}(\delta(i,j) - \langle i(1)j(1)\rangle) \quad . \quad (3)$$

The λ_{ij} are the Lagrange multipliers, only an upper diagonal matrix (i.e., j runs in the interval [i, N/2] only to avoid double summation), and $\delta(i,j)$ is the Kronecker delta. The Lagrangian, L(HF), is also a fourth-order multivariable polynomial of the LCAO coefficients and Lagrange multipliers, i.e., of the set $\{c_{11},\ldots, c_{1K},\ldots, c_{N/2,1},\ldots, c_{N/2,K}, \lambda_{11}, \lambda_{12},\ldots, \lambda_{N/2,N/2}\}$. For example, the one-electron integrals in the closed shell case in Eq.3 is $2\,\Sigma_{i=1}^{N/2}\Sigma_{k1=1}^{K}\Sigma_{k2=1}^{K} c_{i,k1}\, c_{i,k2} \int G_{k1}(1)\, h\, G_{k2}(1) d\mathbf{r}_1$, when one performs the expansion. The nuclear frame and N govern the solutions in agreement with DFT. The evaluation of molecular integrals, $\int G_{k1}(\mathbf{r}_1) G_{k2}(\mathbf{r}_1) d\mathbf{r}_1$, etc., is well known and well documented [4], and these integrals are calculated at the beginning of any computational chemistry programs for Eq.3. Collecting and sorting terms in Eq.3 under the same powers is simple by using, e.g., a FORTRAN embedded do-loop, and optimizing the process to decrease the computation time is essential. Examples are discussed below to provide simple demonstrations.

Statement 1: For closed or open shell one-determinant excited state approximations ($\Psi_k \approx S_k$), the polynomials are analogous to the closed shell case $E_{0,el}$(HF) in Eq.1 or L(HF) in Eq.3; only the LCAO coefficients pick up different values. One must find these local minima of the particular polynomial for excited states. The full concept is presented in Table 1. •

The ROHF, UHF, and KS-DFT methods (as well as some related cases) are analogous to the outlined HF method above, but they are not reviewed here to save space. However, we call attention to a common property of all these methods: Always a particular fourth-order multivariable polynomial comes up (see, e.g., Eq.3) for approximating the ground state energy, and in computational chemistry, it is located with the emblematic SCF algorithm. We do not discuss correlation calculations here, but we mention that the KS-DFT method also falls into this category if the small but not negligible exchange-correlation functional, as correction, is zeroed out (Eq.9). The SCF needs initial values for LCAO coefficients; its theory, stability, and economic programming have been discussed extensively in the literature, along with its applications for millions of molecular systems. Commercial programs are also widely available [5–6]. By contrast, our method differs from the SCF algorithm (indicated in Appendix 8 of [7]). The LCAO coefficients do not need initial (guess) values, and not only the one-determinant approximation of ground state is obtained, but the one-determinant approximation of lowest lying excited states also. The main feature in our work is that we replace the conventional SCF for ground state (App.1): The Lagrangian is treated: a, with the help of Buchberger's algorithm using the Groebner math basis, and b, with the diagonalization of the Hamiltonian matrix from basis functions (Eq.2) followed by the multivariable Newton-slope method. These two are used (alternatively) to obtain one-determinant approximation of ground and excited states. The variation principle holds in the close convex neighborhood of the global and local minima. Relevant remarks are given in App.2.

2. Generalization of the Lagrangian for open- and closed systems, different multiplicities, and excited states

The subject of this chapter for ground states is described extensively in textbooks, but we review it here briefly to extend to excited states. Eqs.1 and 3 are particular cases of even N and all MO with double occupation, (i.e., closed systems with singlet multiplicity). The form of open systems with different multiplicities has also been presented in textbooks for one-determinant approximation of ground state. We extend these to the general case when the Lagrangian is a one-determinant approximation of ground and excited states with any possible multiplicities: When N is even or odd, and one allows any variation for the multiplicities, the discussion is straightforward. Table 1 shows specific examples.

The one-determinant wave function approximation for ground and excited states is $\Psi_k \approx S_k \equiv (N!)^{-1/2} |\sigma_1 f_1(\mathbf{r}_1), \sigma_2 f_2(\mathbf{r}_2), \ldots, \sigma_N f_N(\mathbf{r}_N)\rangle$, wherein σ_i is α (s = ½) or β (s = -½) spin. Obviously, between two different states, when $k \neq k'$, the series of MO functions is different sets: $\{f_1, f_2,\ldots f_N\} \neq \{f_1', f_2',\ldots f_N'\}$, but overlap is possible. Any multiplicity can be modeled with this S_k; for example, a high spin excited state for Li with naïve names for MOs is $(1/3!)|\alpha_1\ 1s(\mathbf{r}_1), \alpha_2\ 2s(\mathbf{r}_2), \alpha_3\ 2p_x(\mathbf{r}_3)\rangle$, while the ground state is $(1/3!)|\alpha_1\ 1s(\mathbf{r}_1), \beta_2\ 1s(\mathbf{r}_2), \alpha_3\ 2s(\mathbf{r}_3)\rangle$. (The naïve names mean that, for example, 1s is now an MO that is very close to the exact atomic orbital but perturbed by other electrons via Coulombic interaction and by other nuclei, if any.) As mentioned above, the HF approximation is the method wherein the orthonormal MOs, the $\sigma_i f_i(\mathbf{r}_i)$, are found, which minimize the $E_{0,el}(HF) \equiv \langle S_0|HS_0\rangle$ with normalization $\langle S_0|HS_0\rangle = 1$ for ground state S_0. More generally, via the immediate consequence of the Schrödinger equation, such as $E_{k,el} = \langle\Psi_k|H_{el}\Psi_k\rangle = E_{k,el}\langle\Psi_k|\Psi_k\rangle$, the minimization of $E_{k,el} \approx E_{k,el}(HF) \equiv \langle S_k|H_{el}S_k\rangle$ finds the global (ground state) and some lowest-lying (limited by the basis set used in Eq.2) local (excited states) minima (stationary points) to approximate the ground (k = 0, global minimum) and excited states (k>0, local minima). Using shorthand notation F_i

$\equiv \sigma_i f_i(\mathbf{r}_i)$, the expansion of $<S_k|H_{el}S_k>$ (p. 7 in [2] for k=0) yields the following (this index k is not to be confused with the one in Eq.2.):

$$E_{k,el} \approx <S_k|H_{el}S_k> = \Sigma_{i=1}^{N} H_i + \tfrac{1}{2} \Sigma_{i=1}^{N} \Sigma_{j=1}^{N} (J_{ij} - K_{ij}) \quad (4)$$

where $H_i \equiv \int F_i^*(\mathbf{x}_1)\, h(\mathbf{r}_1) F_i(\mathbf{x}_1) d\mathbf{x}_1 = \int f_i^*(\mathbf{r}_1)\, h(\mathbf{r}_1)\, f_i(\mathbf{r}_1) d\mathbf{r}_1$ is the one-electron integral with $h(\mathbf{r}_1)$ in App.1, $J_{ij} \equiv \int |F_i(\mathbf{x}_1)|^2 r_{12}^{-1} |F_j(\mathbf{x}_2)|^2 d\mathbf{x}_1 d\mathbf{x}_2 = \int |f_i(\mathbf{r}_1)|^2 r_{12}^{-1} |f_j(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$ is the Coulomb integral, and $K_{ij} \equiv \int F_i^*(\mathbf{x}_1) F_j(\mathbf{x}_1) r_{12}^{-1} F_i(\mathbf{x}_2) F_j^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$ is the exchange integral. The $\mathbf{x}_i = (\sigma_i, \mathbf{r}_i)$ are the spin-orbit coordinates, and the asterisk means complex conjugate, because F_i is generally complex, but in molecular systems, these are real functions. The integrals are real, $J_{ij} \geq K_{ij} \geq 0$, and $J_{ii} = K_{ii}$, coming purely from calculus (based on the form of atomic wave functions and their Gaussian approximations for basis sets), and different multiplicities $(1+\Sigma s_i)$ make different cancellations in K_{ij}. A doubly occupied MO means that, for example, for i = 1 and 2, the $f_1 = f_2$ holds and either $(\sigma_1, \sigma_2) = (\alpha, \beta)$ or $(\sigma_1, \sigma_2) = (\beta, \alpha)$. The one-electron density for the k^{th} state from S_k is $\rho_k(\mathbf{r}_1) = \Sigma_{i=1}^{N} f_i^2(\mathbf{r}_1) \geq 0$ for which $\int \rho_k(\mathbf{r}_1) d\mathbf{r}_1 = N$. The "double standard" notation used here and in computational chemistry literature is highlighted to avoid confusion; in Eqs.10-14, the $f_i \equiv f(\mathbf{r}_i)$ and $g_i \equiv g(\mathbf{r}_i)$ for MOs f and g are functions of $\mathbf{r}_i$, resp., while in Eq.4, f_i denotes the i^{th} MO.

Eq.4 yields the particular cases in Eqs.1 and 3 among the cases upon request. As mentioned above and shown below, Eq.4 always yields a fourth-order multivariable polynomial of the LCAO coefficients for any molecular system. The standard HF-SCF global minimizes Eq.4 for ground state (k = 0); however, using algebraic geometry, we find the local minima (excited states) also beside the global minimum (ground state). The number of lowest-lying excited states is restricted by the highest excited-state (Gaussian-type AO) basis functions used.

We then discuss the contents of Table 1. For simplicity, let N = 5 and 6 be the number of electrons in the molecule, and we fix the nuclear configuration in a single point calculation for these electron configurations. Table 1 demonstrates one-determinant approximations of some ground and excited states. For example, gas phase HF^{5+} and C^+ (N = 5) as well as C and BeH_2 (N = 6), etc. fall into this example. The general cases via Eq.4 are straightforward.

Every column in Table 1 presents a one-determinant configuration. Horizontal rows represent the same MO energy levels: The same order number (i.e., the i in ε_i) may have slightly different energy values in relation to its horizontal neighbors; for example, ε_0(ground) differs from ε_0 (excited state in the second column). If $1/r_{12}$ was neglected in the electronic Hamiltonian operator, then the corresponding horizontal MO energy levels would be the same (i.e., $\varepsilon_{i1} = \varepsilon_{i2}$) for all i would hold between columns (see App.3 and [8-11]). Also, degeneracy is possible, that is, $\varepsilon_i = \varepsilon_j$ for some i and j inside the columns, such as triplet $C(2p_x)$ and $C(2p_y)$, where $\varepsilon_2 = \varepsilon_3$, for example. The ground state is at the global minimum of $L_{N,mult}$, and the excited states are at the local minima of $L_{N,mult}$ at given (N, multiplicity) values. Polynomial $L_{N,mult}$ is the same for horizontal configurations, that is, the same algebraic determinant form (e.g., Eq.3 for L_{61}, as well as the $\{c_{ik}\}$ solutions in Eq.2, distinguish the columns of the given $L_{N,mult}$). The value of a given $L_{N,mult}$ at its different solutions $\{c_{ik}\}$ determines the energy order of excited states among horizontal configurations. For reliable higher excited states, higher (4f, 5g, … etc.) and larger (K in Eq.2) atomic basis sets have to be used. The standard HF-SCF algorithm provides the one-determinant approximation of ground states only by solving Eq.5, that is, the first column in each case in Table 1. However, our algorithm provides the one-determinant approximation of ground and some lowest-lying excited states, that is, any column in Table 1, for example. Our algorithm for Eq.5, which is detailed below for configurations like those in Table 1, suffers from basis set errors and correlation effects as the standard HF-SCF algorithm does, but a related hypothesis is that, for energy differences between columns (i.e., for excitation energies), these two emblematic errors cancel each other out to some degree.

Both, low excited states (changing the electron configurations around HOMO and LUMO MOs) and highly excited states can be calculated with our algorithm by manipulating between lowest-lying MOs. For example, the K_α, K_β, L_α, and L_β characteristic x-ray radiations and Auger electrons can be modeled, for example, for Neon (Z = 10) recall the N = 9 electron Slater determinants for configurations $1s^1 2s^2 2p^6 \rightarrow 1s^2 2s^1 2p^6$ responsible for K_α and K_β radiations. Very high spin (hyper-excitations) calculations are also possible (e.g., for Ne again, the $1s^2 2s^{1\alpha} 2p_x^2 2p_y^2 2p_z^{1\alpha} 3s^{1\alpha} 3p_x^{1\alpha}$, a ↑↑↑↑ state). More details are given in below.

Table 1: Some electronic configurations over a fixed nuclear frame. Using our algorithm, Eq.5 yields their LCAO coefficients to calculate their electronic energy values as multiple solution sets for the horizontal configurations of these three problems distinguished by their Lagrangians. The horizontal configurations are obtained in such a way that two MOs are interchanged in one or more steps with respect to ground state, strictly keeping their contents. It preserves the multiplicity along with the number of singly and doubly occupied MOs, that is, L is horizontally invariant, while vertically is different. For example, in case N = 5, all columns contain exactly two doubly and exactly one single occupied MO. Interchanging the content of two doubly occupied MOs does not change the state, etc..

N= 5, $1+2\Sigma s_i=2$ doublet, polynomial $L_{N,mult}= L_{52}$	ε_4			↑	
	ε_3	LUMO	↑ $\{c_{4k}\}$		
	ε_2	↑HOMO		↑↓	
	ε_1	↑↓	↑↓ $\{c_{2k}\}$		etc.!
	ε_0	↑↓	↑↓ $\{c_{1k}\}$	↑↓	
		ground	excited	excited	excited

N= 6, $1+2\Sigma s_i=1$ singlet, polynomial $L_{N,mult}= L_{61}$	ε_4				
	ε_3		↑↓	↑↓	
	ε_2	↑↓		↑↓	
	ε_1	↑↓	↑↓		etc.!
	ε_0	↑↓	↑↓	↑↓	
		ground	excited	excited	excited

N= 6, $1+2\Sigma s_i=3$ triplet, polynomial $L_{N,mult}= L_{63}$	ε_4		↑	↑	
	ε_3	↑			
	ε_2	↑	↑	↑↓	
	ε_1	↑↓	↑↓	↑	etc.!
	ε_0	↑↓	↑↓	↑↓	
		ground	excited	excited	excited

3. Algebraic geometry Buchberger's algorithm with Groebner basis and diagonalization of the Hamiltonian matrix with Newton slope method to solve our multivariable polynomial systems

The global and local algebraic minima (physically the stationary points) of L for cases such as Eqs.1–3 can be obtained by solving the non-linear polynomial system

$$\{\partial L/\partial c_{ik}=0, \quad \partial L/\partial \lambda_{ij}=0; \quad k= 1,\ldots, K\} \tag{5}$$

App.4 lists some more details for a direct solution. In Eq.5, K is from Eq.2, and if, e.g., closed shell Eq.3 is used, then i, j = 1,…, N/2. Eq.5 becomes a multivariable polynomial system via, e.g., Eq.3, for example. Importantly, Eq.5 is always a third-order algebraic system for molecules by the Coulomb and exchange molecular integrals. Larger molecular systems have a larger set of LCAO coefficients to provide a physically plausible description (special force fields in effect can change the algebraic order). Buchberger's algorithm with Groebner basis solves the polynomial system [12–13] in Eqs.3–5 for all its roots without needing initial values for $\{c_{ik}\}$ from Eq.2, along with using an adequately large basis set [7]. The SCF procedure [1–3] solves Eqs.3–5 only for the global minimum (along with initial values needed) for a one-determinant approximation of the ground state.

All roots of the polynomial system in Eq.5 can be obtained by an algebraic geometry device, which is a mathematical standard; introductions can be found in Chapters 2–3 in [12] and Example 2.3 on p.29 in [14].

Going back to our computational chemistry task, the L (e.g., in Eq.3), what needs to be optimized to obtain the LCAO coefficients and Lagrange multipliers (i.e., the set $\{c_{11},\ldots, \lambda_{11},\ldots\}$ via Eq.5), is generally $L = T + V_{ne} + \Sigma\lambda_{ij}(\delta(i,j) - \int i(1)j(1)) + V_{ee}$, wherein we used the abbreviation of kinetic (T), nuclear-electron attraction (V_{ne}), conditions (λ_{ij}), and electron-electron repulsion (V_{ee}) terms (App.1). The degrees of these four terms are 2, 2, 3, and 4, respectively, and in the multivariable polynomial system to solve in Eq.5, these terms yield 1, 1, 2, and 3 degree terms, respectively, via the derivatives. As described above, Eq.5 can be solved directly with an algebraic geometry device [12, 15] for all solutions; however, numerous solutions are generated (3^m). The latter can be reduced by asking the lowest value Lagrange multipliers λ_{ij} (in using the software, e.g., [15]) corresponding to the lowest-lying states only, and many physically irrelevant complex solutions emerge aside from the important real ones. In this way, the task is finished.

However, the computation part of the optimization can be reduced (Apps.3 and 5) as another choice if in a first step only the $L_{no\ el\text{-}el} = T + V_{ne} + \Sigma\lambda_{ij}(\delta(i,j) - \int i(1)j(1))$ reduced L is used in Eq.5 for the initial guess set $\{c_{11},\ldots, \lambda_{11},\ldots\}$, that is, without V_{ee}. In practice, it yields values very close (roughly 95%–99% in absolute LCAO coefficient) values to the optimal ones established in [8]. Thereafter, adding the V_{ee} term with these initial coefficients gives relatively

good approximations for ground and excited state energies, but chemical accuracy cannot be reached, so it must be refined. First, the system in Eq.5 is reduced to the second order, and solving it is simpler with the direct algorithm above [12, 15–16]; the number of solutions is only maximum 2^m. Second step in this latter procedure is to converge the initial guess set with the ordinary multivariable Newton slope method (App.6) to the optimal coefficients, but now using the full L (i.e., including V_{ee}) as in the direct method. As expected, this process yields the same results in a few (Newton slope) steps as the direct solution. Importantly, the ground (global minimum) and excited states (local minima) can be located with the Newton slope method; that is, the values in the initial guess set, $\{c_{11},\ldots, \lambda_{11},\ldots\}$, from the first step are in the close convex vicinity of minima, a functional analytic property. Again, an adequate Gaussian atomic basis set must be used for Eq.2, and it is a further advantage if all its subsets placed on any atoms are quasi-orthonormal (in the subset). Finally, not two but three strategies (algorithms) are derived, which will be discussed next.

Algorithm 1: Solving the fourth-order Lagrangian, L, with algebraic geometry

The third-order polynomial system in Eq.5 is solved directly with an algebraic geometry device (Buchberger's algorithm using the Groebner math basis, [12, 15], App.4) for all solution sets $\{c_{ik},\lambda_{ij}\}$ for ground and excited states simultaneously, and the corresponding energy values $T + V_{ne} + V_{ee}$ are calculated using $\{c_{ik}\}$. The technical disadvantage to using this algebraic geometry device is that software is not widely available, and a large number of multiple and complex solutions are derived. If the N electrons occupy m different MOs, (e.g., m = N/2 or (N+1)/2 if double occupation is maximal), then the K basis functions in Eq.2 and m(m+1)/2 conditions in Eq.3 yield mK + m(m+1)/2 = m(2K+m+1)/2 variables (unknowns) in the set $\{c_{ik},\lambda_{ij}\}$, generating $3^{m(2K+m+1)/2}$ solution sets, which is a large number. (In Table 1, m = 3, 3, and 4.) Software for this task allows the reduction in the search for the calculation and for the output with restrictions, for example, $abs(c_{ik}) < 2.0$ or $\lambda_{ij} < 0$, etc. The initial guess for LCAO coefficients (c_{ij}) and Lagrange multipliers (λ_{ij}) is not necessary.

Algorithm 2: Solving the Lagrangian, L, without the term V_{ee} with algebraic geometry and finishing with the multivariable Newton slope method

With $L_{no\ el\text{-}el} = T + V_{ne}$ + conditions reduced Lagrangian, the second-order polynomial system in Eq.5 is solved with an algebraic geometry device (as in algorithm 1, [12, 15-16]) for all solution sets simultaneously and used as $\{c_{ik},\lambda_{ij}\}_{initial}$ for ground and excited states. These are in the convex vicinity of minima of L. It yields the first estimate for the corresponding energy value $T + V_{ne} + V_{ee}$ using the $\{c_{ik}\}_{initial}$. (The maximum number of solution sets is only $2^{m(2K+m+1)/2}$ now.) With all essentially different real solutions, one by one, with the multivariable Newton slope method for the full L (Eq.7; see Apps.5 and 6), the parameters are converged in a few steps in the vicinity of local (excited states) and global (ground state) minima to $\{c_{ik},\lambda_{ij}\}_{final}$., and the corresponding final energy values $T + V_{ne} + V_{ee}$ are calculated by using $\{c_{ik}\}_{final}$.

Algorithm 3: Approximate solutions of Lagrangian, L, from diagonalization of the Hamiltonian matrix (accomplished from the basis set), and finishing with the multivariable Newton slope method

The Hamiltonian matrix is diagonalized via Eq.2 with the one-electron operator h (Apps.3 and 7):

$$<G_{k1}(\mathbf{r}_1)|\ h(\mathbf{r}_1)\ |G_{k2}(\mathbf{r}_1)> \quad \text{wherein} \quad h(\mathbf{r}_1) \equiv -\tfrac{1}{2}\nabla_1^2 - \Sigma_{A=1}^{M} Z_A/R_{A1} \tag{6}$$

(Eigenvalues and eigenvectors of Eq.6 with M = 1 atom and with adequate basis functions in Eq.2 approximate the one-electron atom ground and excited states textbook hydrogen-like energies and wave functions, as well as if M>1, these approximate the one-electron system energy levels and wave functions on the given nuclear frame.) Let the eigenvectors with eigenvalues, the $\{c_{i1}, c_{i2}, \ldots, c_{iK}\}$ with ε_i, be ordered as $\varepsilon_{i-1} \le \varepsilon_i$. Apart from that, degeneracies can occur, it is a K*K symmetric real matrix with K eigenvectors and K real eigenvalues via Eq.2. The eigenvectors yield initial values for LCAO coefficients, $\{c_{ik}\}$, in occupied MOs for single or doubly electron occupation, and the eigenvalues yield initial values for Lagrange multipliers $\{\lambda_{ij}\}$. These are the MOs shown in example of Table 1. A state is established to calculate, for example, from Table 1, the N = 5 case with electron configuration in the second column marked with $\{c_{1k}\}$, $\{c_{2k}\}$, $\{c_{4k}\}$ with $\varepsilon_0, \varepsilon_1, \varepsilon_3$. (In energy diagrams like Table 1, the energy level numbering is i = 0, 1, 2, 3,…, while in LCAO coefficients, c_{ik}, the numbering is i = 1, 2, 3, 4,…, and the first indices in c_{ik} can be reordered.) Diagonalization in Eq.6 yields orthogonal scalar products $\{c_{i1}, c_{i2}, \ldots, c_{iK}\}^*\{c_{j1}, c_{j2}, \ldots, c_{jK}\} = \delta_j$. while in Eq.3, the conditions (terms with λ_{ij}) have weighted scalar products, and the weights are the molecule integrals. However, this step is for initial values only. The best result is obtained when the basis set $\{G_k\}$ in Eq.2 is orthonormal

to use in Eq.6; see paragraph at the end of algorithm 3. The theorems in App. 8 show the initial values: $\lambda_{ij,initial}=0$ if $i \neq j$ and ε_i if $i = j$. With this $\{c_{ik},\lambda_{ij}\}_{initial}$, the chosen electron configuration, which is the ground or a particular excited state, its first estimate energy value $T + V_{ne} + V_{ee}$ can be calculated using $\{c_{ik}\}_{initial}$.

The next step uses the multivariable Newton slope method, as in algorithm 2, and it yields the $\{c_{ik},\lambda_{ij}\}_{final}$. The latter provides the final one-determinant energy value $T + V_{ne} + V_{ee}$ with using $\{c_{ik}\}_{final}$. (Eq.6 does not include V_{ee}, whereas Eq.7 does.) With gradient vector G and Jacobian J_G, see App.6; the multivariable Newton slope method in this algorithm is the iteration via (G is not to be confused in Eq.2 vs. Eq.7.)

$$[c_{ik}, \lambda_{ij}]^T_{next} = [c_{ik}, \lambda_{ij}]^T_{previous} - J_G(c_{ik}, \lambda_{ij})^{-1}\, G(c_{ik}, \lambda_{ij}) \qquad (7)$$

Solving Eq.7 is easy if the polynomial (like Eq.3) is available, or alternatively, it can be solved symbolically, for example, see [15] (in which the syntactic command is FindRoot[{$\partial L/\partial c_{11} == 0$, $\partial L/\partial c_{12} == 0$,…}, {{$c_{11}$, $c_{11,ini}$}, … {λ_{mm}, $\lambda_{mm,ini}$}}]); m is the number of MOs. Alternatively, Eq.7, which finishes the convergence, can be replaced with the standard SCF algorithm using the initial LCAO guesses from Eq.6 for ground and excited states. With regard to another theoretical aspect of Eq.6, DFT is based on the fact that the nuclear-electron operator, $-\Sigma_{A=1}^{M} Z_A/R_{Ai}$, determines the electron density along with N. The one-electron operator, $h(\mathbf{r}_i)$ in Eq.6, determines (Apps.1,3, and 5) the approximate (or backbone) solutions for ground and excited states along with N.

We then discuss the orthonormal basis set for Eq.6. Diagonalizing Eq.6 solves the one-electron equation $h(\mathbf{r}_1)\, y_Q = \varepsilon_Q\, y_Q$ with LCAO for ground (Q = 0) and excited states (Q > 0), but $\{G_k\}$ must be orthonormal, which is a purely linear algebraic demand. In practice, the $\{G_k\}$ Gaussian atomic basis set from databases is only normalized for all its elements. It is advantageous if it is near-orthogonal, at least in the subsets located on each individual atom, but the entire set is generally not orthogonal, although G_{k1} and G_{k2}, located on two different atoms, may have near-zero overlaps. Eq.7 corrects everything in the next steps with a quasi-orthonormal $\{G_k\}$. However, orthonormalization can be performed by using the Gram–Schmidt procedure, a standard downward triangular algorithm as $F_1 = G_1$, $F_2 = G_1 + b_2G_2$, etc. In this way, Eq.6 can be applied with replacement $G_k \rightarrow F_k$, and the LCAO coefficients have to be calculated for $\{F_k\}$, not for $\{G_k\}$, to obtain the best initial guess, and Eq.7 needs fewer steps. (The Gram–Schmidt procedure is non-unique, but that is irrelevant in this respect.)

4. Programming complexities and difficulties

Only a few software packages such as WOLFRAM [15] or JULIA can be used for algorithms 1–2. They can solve the systems automatically, without the need for human intervention between input and output or knowledge of the method. However, programming algorithm 3 is almost elementary (eigensolver, matrix inverter). We found that algorithm 1 is theoretically very important and algorithm 3 is the most practical (fast and requires low disk space).

In principle, algorithms 1, 2, and 3 should give the same energy values for the same system and same basis set used up to numerical errors for ground and excited states. Also, for the ground state, the HF-SCF/basis energy is the same. The reason is that the polynomial (e.g., Eq.3) is the same for all three algorithms with well-defined minima; in other words, the task of these algorithms are to locate the minima of the same polynomial. One must keep in mind that the algebraic geometry device, which was fully used in algorithm 1, is for general polynomial systems containing linearly independent equations. However, Eq.5 is not only a linearly independent system, but the equations in it relate to each other, as all equations are from a common Lagrangian, L; recall the concept of mathematical potential functions.

A numerical support is given for algorithms 2 and 3. The (T, V_{ne}, V_{ee}, N) values in Hartree at the HF-SCF/STO-3G level [6] for the hydrogen molecule (H_2) are (1.201985, −3.712036, 0.6752968, 2), and those for naphthalene ($C_{10}H_8$) are (375.3907, −1797.8561, 586.0053, 68). The ratio V_{ee}/(number of electron pairs) is 0.6752968 for hydrogen and $586.0053/(^{68}_{2}) = 0.257246$ for naphthalene. The latter two ratios are of the same magnitude, while the number of electrons (N) is far from the same, and the nuclear frames are completely different. Furthermore, for formaldehyde (CH_2O) $73.05079/(^{16}_{2}) = 0.608757$, for water dimer $92.93053/(^{20}_{2}) = 0.489108$, and so on. The V_{ee}/(number of electron pairs) is not a constant because all electron pairs are under the influence of varying nuclear frames but is a quasi-constant function of nuclear frame [8]. This example supports the idea that the $T+V_{ne}$ is dominant in the minimum search of polynomial L; the V_{ee} behaves roughly as a quasi-constant:

$$V_{ee} \approx a\ (^{N}_{2}) \text{ with } 0.2 < a < 0.7 \;\Rightarrow\; \partial V_{ee}/\partial c_{ik} \approx 0 \quad \text{and} \quad \partial V_{ee}/\partial R_{Au} \approx 0 \qquad (8)$$

(In this way, the "a" is constant between conformers and excited states in this crude approximation.) According to Eq.8, V_{ee} shifts L upward only by approximately leaving the locations of minima; that is, V_{ee} shifts the LCAO coefficients slightly. Eq.8 provides a pre-optimization for electronic energies, $E_{k,el}$, via Eq.5. Pre-optimization for geometry optimization is possible, neglecting the time consuming calculation of V_{ee}. The magnitude [9] of correlation energy and basis set error is $E_{corr} \approx \alpha(N-1)$ with $\alpha = 0.1$ h for STO-3G and $\alpha = 0.039$ h for 6-31G basis set in an N-

electron system, but it non-negligibly depends on nuclear geometry in relation to chemical accuracy. The N-1 comes from the fact that an electron has N-1 neighbor electrons.

5. Extending the algorithm with correlation energy and DFT

The original idea of DFT is that the ground-state electronic energy is a (nonlinear) functional of $\rho_0(\mathbf{r}_1)$ only in the field of the nuclear frame. The multivariable $(s_1, \mathbf{r}_1, .., s_N, \mathbf{r}_N)$ linear differential electronic Schrodinger equation can be reduced to a nonlinear differential equation with only the variable $\mathbf{r}_1$. The dimensionality is reduced as $4N \rightarrow 3$. An innovation of KS-DFT is the development of the form of kinetic operator T(DFT) and V_{ee}(DFT). The corresponding, e.g., closed-shell KS-DFT Lagrangian to the closed-shell HF approximation Lagrangian in Eq.3 is

$$L(DFT) = T(DFT) - \Sigma_{A=1}^{M} \int \rho_k(\mathbf{r}_1) (Z_A/R_{Ai}) d\mathbf{r}_1 + V_{ee}(DFT) + \Sigma_{i=1}^{N/2} \Sigma_{j \geq i}^{N/2} \lambda_{ij} (\delta(i,j) - \int i(1) j(1) d\mathbf{r}_1) + E_{corr}(DFT, k) \quad \&$$

$$T(DFT) \equiv 2\Sigma_{i=1}^{N/2} \int i(1) (-\tfrac{1}{2}\nabla_i^2)\, i(1) d\mathbf{r}_1 \quad \& \quad V_{ee}(DFT) \equiv \tfrac{1}{2} \int \rho_k(\mathbf{r}_1)\, \rho_k(\mathbf{r}_2)\, r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 \qquad (9)$$

The V_{ne}(DFT) term is linear, simple and 100% accurate. Originally, Eq.9 was strictly written for k = 0 ground state with lowest-lying MOs, but the literature always considered that the excited states (k > 0) are analogous. The E_{corr}(DFT, k) is the correlation energy in Eq.9 and is 1%–2% of the electronic energy [1–3] for k = 0 ground state coming from the approximations in T(DFT) and V_{ee}(DFT), but larger than the chemical accuracy (1 kcal/mole). As in Eq.9, the HF approximation in Eq.3 must also be corrected with correlation effect E_{corr}(HF, k) because the one-determinant approximation is not accurate, solely coming from the Coulomb distance operator $1/r_{12}$ in V_{ee}(HF). App. 9 provides more details on this extension.

6. Simple calculations for demonstration

We demonstrate our algorithm in the case of the hydrogen atom (Z = N = 1, open system) and the helium atom (Z = N = 2, closed and open systems) because these are small systems with a few LCAO coefficients only. The complexity of the algorithm is exactly the same for N >> 1 open- or closed-shell molecular systems. Obviously, greater complexity requires greater computation time and disk space. We use a small quasi-orthonormal basis set in Eq.2 [7] (i.e., small K) to reduce the cardinality of set of LCAO coefficients. Ground-state hydrogen atom ($1s^1$, $E_{el,0}$= −1/2 h) and its excited state ($2s^1$, $E_{el,0}$= -1/8 h), ground-state hydrogen molecule ($1s^2$, $E_{el,0}$ = −2.9037240 h by Davidson CI calc.), and ground and excited-state helium atom ($1s^2$, $1s^12s^1$, $2s^2$, 24.6 eV ionization energy) will be calculated. These simple systems allow us to demonstrate our algorithm step by step. These are singlet, doublet, and triplet multiplicities, recall Table 1.

For hydrogen, the spatial MOs, f and g, normalized as $\langle f|f\rangle = \langle g|g\rangle = 1$, the textbook Slater determinant for the doublet multiplicity (S = 2) is (β spin is analogous)

$$S_0 = |\alpha_1 f_1\rangle = \alpha_1 f_1 \quad \text{and} \quad S_1 = |\alpha_1 g_1\rangle = \alpha_1 g_1 \qquad (10)$$

For helium with N = 2 and orthonormalized spatial MO as $\langle f|g\rangle = 0$ and $\langle f|f\rangle = \langle g|g\rangle = 1$, the one-determinant approximation normalized S_k, i.e., $\langle S_k|S_k\rangle = 1$, for ground (k = 0) and excited states (low k = 1, 2…) are

$S_0 = |\alpha_1 f_1, \beta_2 f_2\rangle/\sqrt{2} = (\alpha_1\beta_2 - \alpha_2\beta_1) f_1 f_2/\sqrt{2}$ for S= 1 (singlet, ↑↓) $1s^2$ configuration (11)

$S_k = |\alpha_1 g_1, \beta_2 g_2\rangle/\sqrt{2} = (\alpha_1\beta_2 - \alpha_2\beta_1) g_1 g_2/\sqrt{2}$ for S= 1 (singlet, ↑↓) $2s^2$ configuration (12)

$S_k = |\alpha_1 f_1, \beta_2 g_2\rangle/\sqrt{2} = (\alpha_1\beta_2 f_1 g_2 - \alpha_2\beta_1 f_2 g_1)/\sqrt{2}$ for S= 1 (singlet, $\uparrow^{\downarrow}$, para He) $1s^{1\alpha}2s^{1\beta}$ configuration (13)

$S_k = |\alpha_1 f_1, \alpha_2 g_2\rangle/\sqrt{2} = (\alpha_1\alpha_2)(f_1 g_2 - f_2 g_1)/\sqrt{2}$ for S= 3 (triplet, $\uparrow^{\uparrow}$, ortho He) $1s^{1\alpha}2s^{1\alpha}$ configuration (14)

Eqs.11-12 are algebraically the same, but we treat them according to Table 1. All Slater determinants are normalized in Eqs.10–14 with orthonormal f and g (see the $N!^{-1/2}$ factor for N = 1 and 2). Also, there are β spin equivalents to Eqs.13–14. Experimentally, the ortho helium is more stable (deeper in energy) than the para, similarly to Hund's rule for ground-state atoms; that is, $E_{0,el}$(HF,Eq.11) < $E_{0,el}$(HF,Eq.14) < $E_{0,el}$(HF,Eq.13) is expected from calculation.

6a. Hydrogen atom (N = Z = 1), ground and excited states discussed via algebraic geometry

For hydrogen-like atoms, Eqs.3 and 10 yield the S_k (k = 0, 1) and $\langle S_k|HS_k\rangle$. No electron-electron Coulomb terms exist, so the accurate STO atomic basis functions can be used for f and g as c_1 (1s AO) + c_2 (2s AO) + c_3 ($2p_x$ + $2p_y$ +$2p_z$), wherein the symmetry adapted basis set is shown via c_3 based on the equivalent 2p functions. L is

$$L = (-\tfrac{1}{2}\, c_1^2 - c_2^2/8 - 3\, c_3^2/8)\, Z^2 + (1 - c_1^2 - c_2^2 - 3\, c_3^2)\, \lambda \qquad (15)$$

Statement 2: Eq.15 is the prototype of the idea in this work, a third-order multivariable polynomial for H-like atoms, and can be solved using Eq.5 for ground and excited states, simultaneously. Even in this simplest example,

solving Eq.5 with Eq. 15 requires an algebraic geometry device (Solve[*polynomials==0*] in [15], and [12, 16]). Eq.15 can be treated with the standard literature SCF also, but for ground state only. •

In this simple one-atom case in Eq.15, direct derivation yields the textbook list for atomic wave functions; the basis set is the solution. The minima of L in Eq.15 yield the ground and excited states. For Eq.15, the analytical integrations on STO functions are possible because of the atomic central symmetry in the system, along with the fact that no $1/r_{12}$ term exists, that is, the Slater determinant is a 100% accurate wave function. Given the small size of this system, the atomic number Z survives easily as a parameter in the symbolic integration. Solving the system in Eq.5 for Eq.15 yields four solutions that are pairwise the same aside from signs. The two essentially different solutions in [h] are

$$(c_1, c_2, c_3, \lambda) = (\pm 1,\ 0,\ 0,\ -Z^2/2), \qquad E_{0,el}(1s) = \lambda \tag{16}$$

$$(c_1, c_3, \lambda) = (0,\ \pm 3^{-1/2}\,(1-c_2^2)^{1/2},\ -Z^2/8), \quad E_{1,el}(2s \text{ or } 2p) = \lambda \text{ , it is the mixed } 2p \text{ if } c_2 = 0, \text{ and it is the } 2s \text{ if } c_2 = 1 \tag{17}$$

If we add 3s function as $+c_4$ (3s) in the LCAO for f and g in Eq.10, then Eq.15 is still a third-order polynomial, but aside from Eqs.16-17, more solutions, such as that for 3s, appear, in agreement with the concept of minimal basis size for calculating ground and excited states. Conversely, if one does not use the 1s function in Eq.15, that is, $c_1 = 0$ is forced, then the ground state does not come up from Eq.15; recall the concept of Table 1. An SCF algorithm reaches Eq.16 ground state only, while the algebraic geometry device hits both Eqs.16 and 17.

In relation to Eqs.16-17, the basis set error is sampled next, which is always present in calculations in practice. On STO-2G(1s, 2s) basis set level [7] with f or g = c_1 STO-2G(1s(**r**)) + c_2 STO-2G(2s(**r**)), L is

$$\begin{aligned} L = \lambda\,(1 \ &- 4\,(0.0795772\ \ c_1^2 + 0.00448088\ \ c_1\,c_2 + 0.0795765\ \ c_2^2)\,\pi) - \\ &4.92017\ \ (-0.115483\ \ c_1^2 - 0.0554302\ \ c_1\,c_2 - 0.0175886\ \ c_2^2)\,Z^2 - \\ &4\,(0.0833246\ \ c_1^2 + 0.01619\ \ c_1\,c_2 + 0.0162197\ \ c_2^2)\,\pi\,Z^2 \end{aligned} \tag{18}$$

Given the small size of this system, the atomic number Z survives again as a parameter in Eq.18. Solving the system in Eq.5 for Eq.18 yields four solutions that are pairwise the same; the two wave functions in the pairs differ in factor ±1 only in their LCAO coefficients. The two essentially different solutions in h are (the error ee% uses $E_{k,el} = -1/(2n^2)$ = −0.5 and −0.125, respectively).

$$(c_1, c_2, \lambda) = (0.995118,\ -0.130628,\ -0.485234\ \ Z^2),\ E_{0,el}(1s) = \lambda = -0.485235\ \ Z^2,\ \text{ee\%} = 3.0\ \% \tag{19}$$

$$(c_1, c_2, \lambda) = (0.102651,\ \ 0.991838,\ \ -0.11337\ \ Z^2\ ),\ E_{1,el}(2s) = \lambda = -0.11337\ \ Z^2,\ \text{ee\%} = 9.3\ \% \tag{20}$$

The variation principle holds in Eqs.19–20 as expected, not only for the ground state but also for the excited ones. The virial theorem gives −1.9178 in Eq.19 and −1.9536 in Eq.20, which agrees with the theoretical value of −2. The large ee% error comes from the poor basis set used; for example, using the larger STO-6G basis set [7] yields ee% = 0.3 (not shown).

6b. Helium atom (N = Z = 2), singlet ($1s^2$, $2s^2$, …, etc.), ground, and excited states

The helium atom singlet ground (Eq.7) and singlet excitations (Eq.9) are demonstrated here. Eqs.11 and 12 provide the S_k (k= 0, 1, 2…) and $\langle S_k|HS_k\rangle$ for Eqs.3 and 5. With the use of the STO-6G(1s) and STO-1G(2s) minimal basis set from [7], the LCAO for f or g is c_1 STO-6G(1s) + c_2 STO-1G(2s), and

$$\begin{aligned} L = T + V_{ne} + V_{ee} + \lambda\,(\text{norm} - 1) \quad &\& \quad \text{norm} = c_1^2 - 0.252128\ \ c_1\,c_2 + c_2^2 \quad \& \\ T + V_{ne} = -3.98811\ \ c_1^2 + 0.946543\ \ c_1\,c_2 - 0.877599\ \ c_2^2 \quad &\& \quad E_{k,el}(\text{singlet}) = T + V_{ne} + V_{ee} \quad \& \\ V_{ee} = 1.24499\ \ c_1^4 - 0.110618\ \ c_1^3\,c_2 + 0.73487\ \ c_1^2\,c_2^2 - 0.166389\ \ c_1\,c_2^3 + 0.30058\ \ c_2^4 \end{aligned} \tag{21}$$

In this case, $V_{ee} = \int f_1^2 f_2^2/r_{12}$ and $\int g_1^2 g_2^2/r_{12}$. Solving the system in Eq.5 for Eq.21 yields four solutions that are pairwise the same; the two wave functions in the pairs differ in factor ±1 only in their LCAO coefficients.

First, we use algorithm 1 as a substitute for Eq.21 (fourth-order L) in Eq.5 (third-order system), which yields (c_1, c_2, λ) = (0.972729, −0.139746, 1.63336) and (0.121065, 1.00802, 0.233228) LCAO coefficients, approximating $1s^2$ and $2s^2$, respectively. Finally, the energy $T + V_{ne} + V_{ee}$ is

$$E_{0,el}(1s^2, \text{singlet}\ ^1S_0) \approx -2.77636 \quad \text{and} \quad E_{1,el}(2s^2, \text{singlet}) \approx -0.533952 \tag{22}$$

The λ does not relate so simply to $E_{k,el}$ as in the case of one-electron systems such as Eqs.19–20. The V_{ee} parts in these energies are 1.143 and 0.300721 for $1s^2$ and $2s^2$, respectively. We denote (nomenclature) the excitation index, k, for singlet states only in Eqs.21–22.

Using the third-order $L_{no\ el\text{-}el} = T + V_{ne} + \lambda\,(\text{norm} - 1)$ part of Eq.21 only for Eq.5 yields a second-order system. The two essentially different solutions (algorithm 2) in h are (c_1,c_2,λ) = (1.00116, 0.00950124, 3.9884) approximating $1s^2$, and (0.117647, 1.008, 0.834643) approximating $2s^2$. Yet, both are the hypothetical "V_{ee} neglected" cases. Calculating V_{ee} afterwards with these LCAO initial guesses: $V_{ee}(1s^2) \approx 1.24979$ and $V_{ee}(2s^2) \approx 0.300657$. Adding these afterward yields $E_{0,el}(1s^2, \text{singlet}) \approx -2.73865$ and $E_{1,el}(2s^2, \text{singlet}) \approx -0.533989$. These numbers demonstrate how the LCAO coefficients of hypothetical cases where V_{ee} is neglected are close to the physically plausible cases where V_{ee} is

included. In the next step, the Newton multivariable slope algorithm with these two initial LCAO coefficients and λ sets converges exactly to the same values in five steps as in the previous direct calculation, which yielded Eq.22.

If a larger basis set is used, for example, adding STO-1G($2p_x$, $2p_y$, $2p_z$) to the above minimal basis set, then the next excited state can be approximated beside k = 0 and 1. In this way, algorithm 2 for Eq.5 yields (c_1, c_2, c_3, c_4, c_5, λ) = (0.0713844, 0.676358, 0.428026, 0.428026, 0.428026, 0.0657114) with $E_{2,el}(2p_u^2$, singlet, u = x, y or z) = −0.469716.

Statement 3: The Lagrangian of helium atom with Eq.21 is also the prototype of the idea in this work wherein electron-electron Coulomb interaction is present, a fourth-order multivariable polynomial. It shows all features of our algorithms (specifically, algorithms 1 and 2) to estimate one-determinant approximation for ground and excited states. Larger basis sets or larger molecular systems generate more LCAO coefficients to calculate; however, the polynomial degree remains four. It can be solved via Eq.5 for ground and excited states using algorithms 1–3. Again, L can be treated with the standard HF-SCF also, but for ground state only. •

6c. Helium atom (N = Z = 2), singlet ($1s^2$, $2s^2$,… etc.), ground and excited states with simple correlation estimation

Electronic energies via Eqs.11–12 were calculated above, which resulted in Eq.22. Here, we perform a simple correlation effect that included calculation based on $S_k = (b_1 (\alpha_1\beta_2 - \alpha_2\beta_1) f_1f_2 + b_2 (\alpha_1\beta_2 - \alpha_2\beta_1) g_1g_2)/\sqrt{2}$ for S = 1 (singlet, $\uparrow\downarrow$) $1s^2$ and $2s^2$ configurations. S_k is now a certain CI wave function composed of two determinants with orthonormal {f, g}; see also App.10. If f is a $1s^2$ like MO and g is a $2s^2$ like MO, then Eq.4 cannot be applied directly because that is for one-determinant S_k only. However, the evaluation is straightforward. The $\langle S_k|S_k\rangle = 1$ yields $b_2^2 = 1-b_1^2$. Thus, let us say only the b_1 has to be calculated additionally in Eq.5, which enters as the $\partial L/\partial b_1 = 0$. Alternatively, the $\lambda(-1 + b_1^2 + b_2^2)$ enters in L as an additional Lagrange multiplier. The previous $L_{prev} = 2\langle f_1|h_1|f_1\rangle + \langle f_1f_2|\ 1/r_{12}\ |f_1f_2\rangle + \lambda_{11}(-1+\langle f|f\rangle)$ for Eqs.11–12 yields the LCAO coefficients for f and g by algorithm 3 simultaneously, yielding Eq.22. Now, $L_{next} = \langle S_k|\ H_{el}\ |S_k\rangle + \lambda_{11}(-1+\langle f|f\rangle) + \lambda_{12}(\langle f|g\rangle) + \lambda_{22}(-1+\langle g|g\rangle) + \lambda_{33}(-1 + b_1^2 + b_2^2)$ with $\langle S_k|\ H_{el}\ |S_k\rangle = 2\, b_1^2\langle f_1|h_1|f_1\rangle + 2b_2^2\langle g_1|h_1|g_1\rangle + b_1^2\langle f_1f_2|\ 1/r_{12}\ |f_1f_2\rangle + b_2^2\langle g_1g_2|\ 1/r_{12}\ |g_1g_2\rangle + 2b_1b_2\langle f_1f_2|\ 1/r_{12}\ g_1g_2|\rangle$. If $(b_1, b_2) = (1, 0)$ or $(0, 1)$, then L_{next} reduces to L_{prev}. We discuss it with algorithm 3.

The standard CI calculation sets up the CI Hamiltonian matrix using additional HF-SCF virtual orbitals. Alternatively, via our algorithm 3, it can be accomplished from determinants belonging to Eq.22. Now, f and g are in hand, and for deeper energy, the $\langle f_1f_2|\ 1/r_{12}\ |g_1g_2\rangle$ exchange integral must be calculated. In the next step, the 2 × 2 CI Hamiltonian matrix is $[[\langle S_0|H_{el}|S_0\rangle, \langle S_1|H_{el}|S_0\rangle]^T, [\langle S_0|H_{el}|S_1\rangle, \langle S_1|H_{el}|S_1\rangle]^T] = [-2.77636, \langle f_1f_2|\ 1/r_{12}\ |g_1g_2\rangle]^T, [\langle f_1f_2|\ 1/r_{12}\ |g_1g_2\rangle, -0.533952]^T]$, and its eigenvalues are correct (e.g., Eq.22). Finally, f and g are obtained from L_{prev} with algorithm 3, or MOs and virtual MOs from a standard HF-SCF/basis calculation, followed by eigensolving the Hamiltonian matrix to refine Eq.22. In sum, algorithm 3 is used for L_{prev} followed by an eigensolver for refinement.

Alternatively, to ensure an accurate result, f and g can be optimized using L_{next} directly. Lower energy can be obtained than that obtained by the standard CI method in the previous paragraph. By the term $2b_1b_2\langle f_1f_2|\ 1/r_{12}\ g_1g_2|\rangle$, the L_{next} is not a fourth, but as sixth-order multivariable polynomial; however, it should not be a problem in algorithm 3. It is the case also if more determinants, S_0, S_1, S_2, … , are used. Initial LCAO values for L_{next} can be obtained from Eq.6, (similarly as for L_{prev}). $E_{0,el}(HF, 1s^2) = -2.77636$ in Eq.22, (and it is the same with using basis set {STO-6G(1s), STO-1G(2s,$2p_u$, u=x, y, z)} or with {STO-6G(1s), STO-1G(2s)}, because the larger basis set is extended with orthogonal basis functions only [7]). Using algorithm 3 for L_{next} yields $E_{0,el}(HF$ with $E_{corr}, 1s^2) = -2.85837$, a positive improvement. The initial value $(b_1,b_2) = (1,0)$ leads to ($E_{0,el}$(HF with E_{corr}, $1s^2$), and (0,1) leads to ($E_{1,el}$(HF with E_{corr}, $2s^2$). Together, algorithm 3 is used directly for richer L_{next} in one step, which accounts for a part of the correlation effect.

6d. Para helium atom (N = Z = 2), singlet ($1s^{1\alpha}2s^{1\beta}$,…, etc.), ground, and excited states

Didactically, He($1s^2$) is the real ground state. For para helium (here) and ortho helium (next), the term "ground state" is restricted to their spin condition and singly occupied MO situation (App.1). We do not discuss the allowed electric dipole transitions, only the energy levels, and we do not use the atomic term symbols but the electronic configurations.

The one-determinant approximation for the ground and excited state wave functions of the para helium atom is presented in Eq.13. Using the {STO-6G(1s), STO-1G(2s)} minimal basis set [7], the LCAO for two singly occupied MOs, f(**r**) and g(**r**), are c_{i1} STO-6G(1s) + c_{i2} STO-1G(2s) with i = 1, 2. The electronic energy is $\langle S_k|\ H_{el}\ |S_k\rangle = \langle f_1|\ h_1\ |f_1\rangle + \langle g_1|\ h_1\ |g_1\rangle + \langle f_1^2|\ 1/r_{12}\ |g_2^2\rangle$ after integrating the spins (α, β) out, and the last term is $V_{ee} = J_{12} = \int f_1^2 g_2^2/r_{12} = \int f_2^2 g_1^2/r_{12}$ in accord with Eq.4. The Lagrangian, L(HF), is derived by adding $\lambda_{11}(-1 + \langle f_1|f_1\rangle) + \lambda_{12}\langle f_1|g_1\rangle + \lambda_{22}(-$

$1+\langle g_1|g_1\rangle$) to the electronic energy expression. With this minimal basis set, we use the first step only in algorithm 2 as a weaker approximation and algorithm 1 for comparison. Using the first step in algorithm 2 and solving the system in Eq.5 for $L_{no\ el\text{-}el}$ yields 16 real solutions (see syntactic, e.g., in App.4), which are essentially two different solutions only. (Algebraic multiplicities among the 16 ones come from some alternating signs, and the content of f and g can be interchanged.) Thus, without V_{ee}, an LCAO vector is (λ_{11}, λ_{12}, λ_{22}, $c_{11}, c_{21}, c_{12}, c_{22}$) = (1.98663, −0.217969, 0.42489, 0.990599, −0.186725, −0.0603562, −1.00623), for example. Adding V_{ee} thereafter yields −2.02305 and −1.8746 h ground and excited state singlets, originating from the alternating sign in c_{ik}, e.g., 0.990599, −0.0603562 (weakening) vs. 0.990599, 0.0603562 (amplifying). The latter energy is a weak approximation for $1s^{1\alpha}2p_u{}^{1\beta}$. The more realistic approximation is when V_{ee} is involved in L for Eq.5, and algorithm 1 yields the two essentially different (c_{11}, c_{21}, c_{12}, c_{22}, singlet electronic energy, naïve configuration) solution vectors as

(0.0247145, 1.00774, −0.996584, 0.151557, −2.05972 h, $1s^{1\alpha}2s^{1\beta}$)

(0.695105, 0.730056, 0.811859, −0.597525, −1.84078 h, $1s^{1\alpha}2p_u{}^{1\beta}$)

Using the larger basis set, {STO-6G(1s), STO-1G(2s), STO-1G($2p_u$, u=x,y,z)}, the indices in LCAO coefficients (Eq.2) and Lagrange multipliers run as in vector (λ_{11}, λ_{12}, λ_{22}, c_{ik}, i = 1, 2 and k = 1 to 5), yielding a large number of solutions (max. $1*1*1*3^{10} \approx 60000$, including multiples and complexes) for the system Eq.5 via algorithm 1, even if one reduces it with the three equivalent $2p_u$ as $c_{i3} = c_{i4} = c_{i5}$ with i = 1 and 2. Moreover, the computation time is still long in pre-calculation wherein the V_{ee} is neglected (first step in algorithm 2). However, the diagonalization of the Hamiltonian matrix in Eq.6 (algorithm 3) is fast and yields eigenvalues ($\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5$) = −2.029261, −0.403592, −0.452706, −0.452706, −0.452706, and eigenvectors (y_1, y_2, y_3, y_4, y_5) = ([0.989112, −0.147164, 0,0,0]^T, [0.147164, 0.989112, 0, 0, 0]^T, [0, 0, 1, 0, 0]^T, [0, 0, 0, 0, 1, 0]^T, [0, 0, 0, 0, 0, 1]^T), corresponding to atomic 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals via the basis set. These are rough but good initial LCAO coefficient values; the first two eigenvectors yield the first estimate of the para helium ground state singlet ($1s^{1\alpha}2s^{1\beta}$) energy, −2.05936 (including the V_{ee} = 0.373491 thereafter). From Eq.6, the excitation energy is −2.05936 −(−2.77636) = 0.717 h = 19,51 eV. The experimental value is about 20 eV, an excellent agreement. More accurately, the experimental excitation energies are 19.80 eV for He($1s^2$) → ortho helium (triplet $1s^{1\alpha}2s^{1\alpha}$), and 20.61 eV for He($1s^2$) → para helium (singlet $1s^{1\alpha}2s^{1\beta}$). For more accurate values, we finish (converge) it with the second step in algorithm 3 after Eq.5 (i.e., with the Newton slope method), wherein we include the expression of V_{ee}. We use the initial values just described; the outcome is almost instant computationally. (See, e.g., syntactic FindRoot[{D[L, {λ_{11}, 1}] == 0, … D[L, {c_{25}, 1}] == 0}, {{λ_{11}, initial value}, …{ c_{25}, initial value}}] in ref.[15] for this last task.) For ground and excited states, we use the spirit of Table 1; that is, for singlet para He, the one-determinant (Slaterian) wave functions are $|\alpha(1)y_p(1), \beta(2)y_q(2)\rangle$ with p, q = 1, 2, 3, 4, 5 and p ≠ q. Because interchanging the rows of a determinant yields the same absolute value, let p < q. The second part of algorithm 3, the Newton slope to finish, was run for all (p,q) cases individually. Table 2 shows the numerical results.

Table 2: Ground and excited state para helium atom (2^1S_0, 2^1P_1, etc.). The (p, q) means that the Slater determinant is accomplished using eigenvectors y_p and y_q via the Hamiltonian matrix in Eq.6. The algorithm used in this work allows us to estimate many highly excited-state one-determinant wave functions with energies ($E_{k,el}$) for any but fixed multiplicity. The index k is not specified, although arbitrarily, it could be, for example, k = 1, 2, …10 for the (p, q) cases listed, but one must not forget that ortho helium also has a series of energy values; see Table 3. The u, v = x, y, z, and dgnr = degenerate states.

(p, q)	Naïve configuration of para He	Electronic energy, $E_{k,el}$(HF) [h]	$V_{ee} = J_{12}$ [h] involved in $E_{k,el}$(HF); K_{12}=0
(1,2)	$1s^{1\alpha}2s^{1\beta}$	-2.05973	0.35179
(1,3), (1,4), (1,5); dgnr	$1s^{1\alpha}2p_u{}^{1\beta}$	-1.99942	0.44743
(2,3), (2,4), (2,5); dgnr	$2s^{1\alpha}2p_u{}^{1\beta}$	-0.548075	0.322017
(3,4), (3,5), (4,5); dgnr	$2p_u{}^{1\alpha}2p_v{}^{1\beta}$	-0.561294	0.344119

We used low quality basis functions [7] in our demonstrations to have a smaller output of details to exhibit; this causes $\varepsilon_2 \neq \varepsilon_3 = \varepsilon_4 = \varepsilon_5$ instead of $\varepsilon_2 = \varepsilon_3 = \varepsilon_4 = \varepsilon_5$ for initial values (one-electron energies) in this example. The errors [7] in STO-6G(1s), STO-1G(2s), and STO-1G(2pu) are 0.3%, 12.2%, and 9.5%, respectively. The relatively large difference between 12.2% and 9.5% is due to the fact that −0.548075 > −0.561294 in Table 11, that is, $2s^{1\alpha}2p_u{}^{1\alpha}$, is above $2p_u{}^{1\alpha}2p_v{}^{1\alpha}$ energetically, although the reverse energy order is expected (for N > 1 the $2p_u$ is above 2s in the energy diagram, a known energy split). As a comparison, the $E_{1,el}(2s^2$, singlet) ≈ −0.533952 value in Eq.6 is close to

the values −0.548075 and −0.561294 in Table 2, as expected, being both electrons in n = 2 main quantum number state in these cases.

6e. Ortho helium atom (N = Z = 2), triplet ($1s^{1\alpha}2s^{1\alpha}$, …, etc.), ground and excited states

The one-determinant approximation for the wave function of ortho helium atom ground and excited states is given in Eq.14. Similarly to the para helium above, using the same larger basis set, {STO-6G(1s), STO-1G(2s), STO-1G(2pu, u = x, y, z)}, the indices in LCAO coefficients (Eq.2) and Lagrange multipliers run as in vector (λ_{11}, λ_{12}, λ_{22}, c_{ik}, i = 1, 2 and j = 1 to 5). Eq.6 in algorithm 3 yields the same eigens for ortho and para helium because the same basis set is used. The Lagrangian is L(HF) = $\langle f_1|\, h_1\, |f_1\rangle + \langle g_1|\, h_1\, |g_1\rangle + \langle f_1^2|\, 1/r_{12}\, |g_2^2\rangle - \langle f_1 g_1|\, 1/r_{12}\, |f_2 g_2\rangle + \lambda_{11}(-1 + \langle f_1|f_1\rangle) + \lambda_{12}\langle f_1|g_1\rangle + \lambda_{22}(-1+\langle g_1|g_1\rangle)$ after integrating out for (the only α) spins, wherein $V_{ee} = J_{12} - K_{12} = \int f_1^2 g_2^2/r_{12} - \int f_1 g_1 f_2 g_2/r_{12}$. The exchange integral, K_{12}, enters in V_{ee} with a minus sign (Eq.4) indicating that the energy levels of ortho helium are lower (more stable) than those of para helium. ($K_{12} = 0$ in para helium, and $K_{12} \neq 0$ in ortho helium solely by their spin configurations, a case of a general trend that proves Hund's rule on the HF level [2].) Analogously to the para case, we finish (converge) it with algorithm 3 for Eq.5 (i.e., with the Newton slope method wherein we include the expression of V_{ee}); the sources of error are also analogous. Table 3 shows the numerical results.

Table 3: Ground- and excited-state ortho helium atom (2^3S_1, 2^3P, etc.). The (p, q) values are analogous to the ones in Table 2. The index k is not specified; see the caption of Table 2. The u, v = x, y, z, and dgnr = degenerate states.

(p, q)	Naïve configuration of ortho He	Electronic energy, $E_{k,el}$(HF) [h]	$V_{ee} = J_{12} - K_{12}$ [h]	J_{12} [h]	K_{12} [h]
(1,2)	$1s^{1\alpha}2s^{1\alpha}$	-2.06102	0.3505	0.418346	0.0678457
(1,3), (1,4), (1,5); dgnr	$1s^{1\alpha}2p_u{}^{1\alpha}$	-2.01912	0.427009	0.447085	0.0200754
(2,3), (2,4), (2,5); dgnr	$2s^{1\alpha}2p_u{}^{1\alpha}$	-0.612929	0.257876	0.322362	0.0644862
(3,4), (3,5), (4,5); dgnr	$2p_u{}^{1\alpha}2p_v{}^{1\alpha}$	-0.585302	0.320113	0.344121	0.0240084

A comparison of Tables 2 and 3 shows that any triplet (ortho) is lower in energy than the corresponding (same (p,q) value) singlet (para) in accordance with experiments. The $2s^{1\alpha}2p_u{}^{1\alpha}$ is lower in energy ($E_{k,el}$) than the $2p_u{}^{1\alpha}2p_v{}^{1\alpha}$ in Table 3, as expected. A comparison of the lowest-lying para and ortho helium ((p,q) = (1,2)) in Tables 2 and 3), as simplified in textbooks, shows that the energy difference comes from $K_{12} = -0.0678457$ h = −1.846 eV. The difference of the two $E_{k,el}$ from Tables 2 and 3 is −2.06102 −(−2.05973) = −0.00129 h = −0.035 eV, a more plausible calculation. The experimental energy difference is 19.8 (ortho) − 20.6 (para) = −0.8 eV (using helium ground state as reference). The K_{12} overestimates, and the difference in $E_{k,el}$ values underestimates the absolute value of the 0.8 eV gap in our weak basis set calculation.

Comparing electronic energies of He($1s^2$) in Eq.6, para helium in Table 2, and ortho helium in Table 3 with Spartan [5] (wherein only the first excited state is available and multiplicity specification in the input of the code is not as free as in this work) shows that the latter yields −2.8077840 on RHF-SCF/ STO-3G/singlet, −2.8356799 with RHF-SCF/ 3-31G*/singlet, −2.8551604 on RHF-SCF/ 6-31G*/singlet, and −2.9070483 on DFT-B3LYP/ 6-31G*/singlet level for He($1s^2$), as well as −1.3993078 on UHF-SCF/6-31G*/triplet, and −1.4158561 on DFT-B3LYP/6-31G*/first excited state (TDDFT)/triplet level for ortho He($1s^{1\alpha}2s^{1\alpha}$).

The spin-isomers of para helium are the pairs ($1s^{1\alpha}2s^{1\beta}$, $1s^{1\beta}2s^{1\alpha}$), ($1s^{1\alpha}2p_u{}^{1\beta}$, $1s^{1\beta}2p_u{}^{1\alpha}$), etc., the spin-isomers of ortho helium are the pairs ($1s^{1\alpha}2s^{1\alpha}$, $1s^{1\beta}2s^{1\beta}$), ($1s^{1\alpha}2p_u{}^{1\alpha}$, $1s^{1\beta}2p_u{}^{1\beta}$), etc.. The pairs energetically degenerate, and only one of the pairs were discussed above.

6f. Emblematic electron excitations in relation to our algorithms

The ortho helium → helium and para helium → helium are in fact $K_{\alpha 2}$ and $K_{\alpha 1}$ characteristic x-ray radiation processes, respectively. For example, for the latter, Eq.6 and Table 2 yield −2.77636 − (−2.05973) = −0.71663 h = −19.5005 eV, a weak basis approximation for the experimental 24.6 eV. More generally and for the sake of brevity, in relation to Eq.6, we estimate K_α using a better basis set: We neglect V_{ee} based on the configurations $1s^1 2s^2 2p^6$[electrons at higher levels] and $1s^2 2s^1 2p^6$[electrons at lower levels] having about the same V_{ee}, which cancels out the energy difference. In Tables 2 and 3, $E_{k,el}$ drastically changes, whereas V_{ee} does not. In this approximation,

$K_{\alpha 1}$ and $K_{\alpha 2}$ cannot be distinguished because the exchange integrals (K_{ij}) are not calculated; however, an average K_α is estimated. If the exact orthonormal one-electron atomic Slaterian wave functions are used as a basis set (and LCAO coefficients do not correct, see Apps.3–5), the energy difference (for the average K_α) is ($\varepsilon(1s) + 2\ \varepsilon(2s) + (2\ \varepsilon(2p_x)$ + electron higher than $2p_x$)) - ($2\ \varepsilon(1s) + \varepsilon(2s) + (2\ \varepsilon(2p_x)$ + electron higher than $2p_x$)) = $-\varepsilon(1s) + \varepsilon(2s) = Z^2/2 - Z^2/(2*2^2)$ = $3\ Z^2/8$ h = $10.2043\ Z^2$ eV. This finding agrees with Moseley's empirical law ($10.2\ (Z-1)^2$ eV based on the Lyman–Balmer series hydrogen spectral series of transitions) concerning the characteristic X-rays emitted by atoms wherein the value of −1 is empirically fitted. Through this estimation approach, the (Z (atom), experimental $K_{\alpha 1}$ (uncertainty %), % error of $10.2043\ Z^2$, % error of Moseley's law) values are, for example, (10 (Ne), 848.61 eV (3.1%), −20.2%, 2.6%), (30 (Zn), 8615.823 eV (0.8%), −6.6%, 0.4%), (60 (Nd), 37360.739 eV (0.2%), 1.7%, 4.9%), and (92 (U-238), 94650.84 eV (0.06%), 8.7%, 10.7%). In summary, this calculation (which avoids the non-negligible relativistic effect at Z > about 18) shows that the initial guess from Eq.6 is plausible. This paragraph deals with core electron excitations.

In chemical reactions and spectroscopy, the valence electron rearrangements and excitations (recall the definitions of HOMO and LUMO) play a role, and quantum chemical calculations provide descriptions, explanations, and predictions. Table 1 shows how one can manipulate Slater determinants and how calculations, e.g., for laser energy diagrams can be made. For example, in He-Ne laser, the excitations by electron collisions with helium atoms yield ortho and para helium followed by He-Ne collisions, and the de-excitations from the 3s, 3p, 4s, 4p, and 5s orbitals of the Ne atom provide laser radiation. Algorithm 3 can also be used to describe these problems.

7. Vertical flow diagram of algorithms 1–3 for brief review and summary

Table 4: Chart of steps in our three algorithms. A fourth-order multivariable polynomial of LCAO coefficients (e.g., Eq.3) has well-defined minima; thus, the three algorithms are supposed to yield the same results up to numerical errors. See the Conclusions at the end of this work how they relate to each other.

Algorithm 1	Algorithm 2	Algorithm 3
For the 4th order, e.g., Eqs.3, 21, $L = T + V_{ne} + V_{ee} + \Sigma_i\Sigma_j\ \lambda_{ij}(\delta(i,j) - \int i(1)j(1))$ solve the 3rd order system in Eq.5 with Buchberger's algorithm to get all solution sets $\{c_{ik},\lambda_{ij}\}_{final}$ for ground and excited states for a fixed configuration on demand, e.g., triplets in Table 1.	For the 3th order, e.g., Eqs.3, 21, $L_{no\ el\text{-}el} = T + V_{ne} + \Sigma_i\Sigma_j\ \lambda_{ij}(\delta(i,j) - \int i(1)j(1))$ solve the 2rd order system in Eq.5 with Buchberger's algorithm to get all solution sets $\{c_{ik},\lambda_{ij}\}_{initial}$ for ground and excited states for a fixed configuration on demand, e.g., triplet in Table 1.	Transform the basis set $\{G_k\}$ in Eq.2 to orthonormal basis set with Gram-Schmidt procedure (if it is not-orthonormal or quasi-orthonormal only).
↓	One by one, using the Newton slope method (Eq.7) for the full $L = T + V_{ne} + V_{ee} + \Sigma_i\Sigma_j\ \lambda_{ij}(\delta(i,j) - \int i(1)j(1))$ get the $\{c_{ik},\lambda_{ij}\}_{final}$ from $\{c_{ik},\lambda_{ij}\}_{initial}$.	Diagonalize the Hamiltonian matrix in Eq.6 to get K eigenvectors (LCAO coefficients of i^{th} MO, ϕ_i) with eigenvalues (i^{th} MO energy); V_{ee} is not in effect yet: $\{c_{i1}, c_{i2}, \ldots, c_{iK}\}_{initial}$ with ε_i, ordered as $\varepsilon_{i-1} \le \varepsilon_i$. Set up Lagrange multipliers as $\lambda_{ij,initial} = 0$ if $i \neq j$ and ε_i if $i = j$.
↓	↓	Set up the one-determinant wave function approximation for configuration and excitation on demand (Table 1), e.g., for an N= 4 electron system a triplet ground state is $\lvert\alpha\phi_1, \beta\phi_1, \alpha\phi_2, \alpha\phi_3\rangle$, or a highly excited singlet is $\lvert\alpha\phi_8, \beta\phi_8, \alpha\phi_9, \beta\phi_9\rangle$. Construct the L as in Eq.3.
		Using the Newton slope method (Eq.7) for $L = T + V_{ne} + V_{ee} +$

↓	↓	$+ \Sigma_i\Sigma_j \lambda_{ij}(\delta(i,j) - \int i(1)j(1))$ get the $\{c_{ik},\lambda_{ij}\}_{final}$ from $\{c_{ik},\lambda_{ij}\}_{initial}$.
For the energy values choose one or more $\{c_{ik}\}_{final}$		
Calculate $E_{n,el} = T + V_{ne} + V_{ee}$, DONE		

Appendix

Appendix 1: The electronic non-relativistic Schrödinger equation for a fixed nuclear frame is $H_{el}\,\Psi_k \equiv (\Sigma_{i=1}^{N} h(\mathbf{r}_i) + H_{ee})\,\Psi_k = E_{k,el}\,\Psi_k$ with $E_{k,tot} = E_{k,el} + V_{nn}$ for ground ($k = 0$) and excited ($k > 0$) states, where $h(\mathbf{r}_i) \equiv -\frac{1}{2}\nabla_i^2 - \Sigma_{A=1}^{M} Z_A/R_{Ai}$ is the one-electron operator, $H_{ee} = \Sigma_{i=1}^{N}\Sigma_{j>i}^{N} 1/r_{ij}$ is the Coulomb electron-electron repulsion operator, and $V_{nn} \equiv \Sigma_{A=1}^{M}\Sigma_{B>A}^{M} Z_A Z_B/R_{AB}$ is the Coulomb nuclear-nuclear repulsion energy with distances $R_{AB} \equiv |\mathbf{R}_A - \mathbf{R}_B|$ and $R_{A1} \equiv |\mathbf{r}_1 - \mathbf{R}_A|$. In Eq.1, i and j denote the $i(1) \equiv i(\mathbf{r}_1)$ and $j(1) \equiv j(\mathbf{r}_1)$ spatial functions of MOs for maximum pairwise occupation. The normalized Slater determinants allow us to treat $E_{k,el}(HF) = \langle S_k|H_{el}|S_k\rangle$ instead of $E_{k,el}(HF) = \langle S_k|H_{el}S_k\rangle/\langle S_k|S_k\rangle$. The energy optimization to obtain the LCAO coefficients via integrals $\langle S_k|H_{el}|S_k\rangle$ is, in fact, a least squares fit.

Gaussian basis sets are used to make the evaluation of molecular integrals feasible because the multiplication and derivation of Gaussians are also Gaussians, along with the denominators $z = r_{12} \equiv |\mathbf{r}_1 - \mathbf{r}_2|$ or $z = R_{C1} \equiv |\mathbf{R}_C - \mathbf{r}_1|$, which can be transformed as Gaussian multipliers into the nominator with $z^{-1} = \pi^{-1/2} \int_{(-\infty,\infty)} \exp(-z^2t^2)\,dt$.

According to the square ($\underline{\mathbf{S}}^2$) and z component ($\underline{\mathbf{S}}_z$) total spin operators [1], the wave function (Ψ_k) is an eigen function of both, and its single determinant approximation (S_k) should also be one. The closed-shell single Slater determinant is an eigen function of both, i.e., a pure singlet, a positive property. However, an open-shell single Slater determinant is an eigen function of $\underline{\mathbf{S}}^2$ only if all open shell electrons have parallel spin. The latter at least includes the important cases when only one MO is singly occupied in the system. The ortho helium (two parallel spins) satisfies this property, whereas the para helium (the two spins are not parallel) does not. The names may come from organic chemistry (e.g., ortho vs. para benzene).

For the ground state, we refer to the Slater determinant constructed from the lowest lying MOs; the SCF addresses this issue. For example, the singlet and triplet neutral carbon atoms are both ground state in this way. According to Hund's rule, the triplet is the ground state only because it is energetically on a lower level.

Appendix 2: The multivariable polynomial of variable set $\{c_{ik}\}$, which are the physical LCAO coefficients (see Eq.3) on a chosen basis set $\{G_k\}$ level (Eq.2), determines the global and local minima. The user selects the method: the SCF for global minimum (ground state) or the algebraic geometry device (this work) for all lowest-lying minima (ground and lowest-lying excited states). In principle, the accuracy is the same for the ground state, and only the device used to find the LCAO coefficients differs. On the convergence by conventional SCF for global minimum vs. solving the polynomial for lowest-lying minima with an algebraic geometry device, the former is a one-determinant approximation for ground state ($k = 0$), while the latter simultaneously yields the one-determinant approximation for ground ($k = 0$) and lowest-lying excited states ($k > 0$). The accuracy of the two choices for ground state (global minimum of the polynomial) is the same on the same basis level up to numerical errors. The popular STO-mG type basis set can be picked for Eq.2, for example, from the many available in literature.

Subroutines to calculate molecular integrals for cases (e.g., in Eq.3) are well established and available in computational chemistry workshops [5–6] for program writers/exchange. Sophisticated commercial software is available to treat polynomials for these cases to find their minima [15]. Therefore, reproducing the algorithms in this work is possible.

The minima of, e.g., Eq.3 comes from the derivatives of L; see Eq.5, which yields a third-order multivariable polynomial system. The simplest related 1D algebraic problem is to find all three solutions of the third-order one-variable algebraic equation with the Cardano formula for cubic equations. Solving a system like Eq.5 is a well-known issue in algebraic geometry but has not been applied in computational chemistry practice yet. The standard algebraic solution for general second, third, and higher degrees is available commercially [15].

The SCF can suffer from convergence problems when used for larger molecular systems, and, for example, Pulay's DIIS procedure is used to avoid this problem and to accelerate SCF convergence. Meanwhile, the algebraic geometry device to solve the key system Eq.5 is much more stable. The matrix of LCAO coefficients (e.g., from Eq.3), which is not a square matrix generally, is extended to a square matrix in HF-SCF with the help of virtual MOs for algebraic treatments; this extension is irrelevant in our algorithm. We do not summarize the existing developments in algebraic geometry in this respect; for our purpose, it is enough that it is available or can be programmed. We describe and emphasize the advantage of its use in computational chemistry.

Appendix 3: Instead of the electronic Schrödinger equation in App.1 and instead of L in Eq.3, part of it is solved only as the first step [8–11]; the simple one-electron equation with no electron-electron repulsion $h(\mathbf{r}_1)\, y_k(\mathbf{r}_1) = \varepsilon_k\, y_k(\mathbf{r}_1)$ is solved for k = 0, 1, 2, ..., k_{max} for k_{max} > (even N)/2, ((odd N)+1)/2, etc. Table 1 explains why we need larger k_{max}. With LCAO approximation from Eq.2 for y_k, the Hamiltonian matrix $\langle G_{k1}|h\, G_{k2}\rangle$ must be diagonalized; its eigenvectors are y_k, and the eigenvalues are the corresponding ε_k. From the linear Hermetic operator and the symmetric matrix, the orthonormal property $\langle y_{k1}|y_{k2}\rangle = \delta_{k1,k2}$ holds and the eigenvalues are real. (Basis set in Eq.2, the $\{G_k\}$, must be orthonormal; as well as index k in y_k and G_k are not to be confused!) Using the orthonormalized solution set $\{y_k,\varepsilon_k\}$, similarly to Eqs.10–14, the N electron Slater determinant (now Y_k) solution can be accomplished for $\Sigma_{i=1}^{N} h(\mathbf{r}_i)Y_k = e_k Y_k$ with k= 0, 1, 2, 3,…, and $e_k = \Sigma_{occupied}\, \varepsilon_k$. (For example, for a ground-state Li atom, the $e_0 = 2\varepsilon_0 + \varepsilon_1$.) Recall the basic theorem in DFT, such as the one-electron density is determined uniquely by H_{ne}, so the Y_k is a strong approximation (or initial value), e.g., for Eq.3. It instantly provides [10] a rough approximate $E_{0,el} < E_{0,el}(HF) < \langle Y_0|H_{el}Y_0\rangle/\langle Y_0|Y_0\rangle = e_0 + \langle Y_0|H_{ee}Y_0\rangle/\langle Y_0|Y_0\rangle$ for ground-state electronic energy as a "good, but not totally" converged wave function toward S_0. (The orthonormal property provides $\langle Y_0|Y_0\rangle = 1$.) The $\langle Y_{k1}|Y_{k2}\rangle = \delta_{k1,k2,}$ holds also. The Y_k ground and excited states, obtained in this way, lack the electron-electron repulsion (if one does not add the $\langle Y_k|H_{ee}Y_k\rangle$ term thereafter), but their LCAO coefficients are very close to the vicinity of the global energy minimum (k = 0) and local energy minima (k > 0) in the multidimensional LCAO Cartesian space, depending on how Y_k is accomplished on request (Table 1). With the use of Eq.2, the dimension of this Cartesian space of LCAO coefficients is KN/2 in the case of Eq.3, for example; (N is even in Eq.3). The components of the y_k eigenvectors provide the first guesses (for the corresponding MOs) to find the final LCAO coefficients for ground and excited states. It also needs one more step to find the final (slightly different) LCAO coefficients (Eq.7, App.6).

Appendix 4: Eq.5 can be solved directly for all solution sets after L has been set up, for example, with the Wolfram [15] package with syntax Solve[D[L,{c_{11},1}] == 0, && … D[L,{$c_{N/2,K}$,1}]==0, && D[L,{λ_{11},1}] == 0, && … D[L,{$\lambda_{N/2,N/2}$,1}] == 0, {c_{11},… ,$\lambda_{N/2,N/2}$}, Reals]. In comparison with the standard literature SCF device, one does not need the concept of "virtual orbitals", the initial estimation of LCAO coefficients, and the necessity of the so-called DIIS convergence accelerating and stabilizing device. The L is a fourth-order multivariable polynomial in c_{ik} and λ_{ij}, (see e.g., Eq.3), and $\lim_{cik\to\infty} L = \infty$, as well as Eq.5 reduces it to a third-order multivariable polynomial system of LCAO coefficients containing monomials c_{ik}, $c_{i1k1}c_{i2k2}c_{i3k3}$, $\lambda_{i1j1}c_{i2k2}$, and $c_{i1k1}c_{i2k2}$. In this way, the final LCAO coefficients for ground and excited states can be obtained. Decreasing the order of the polynomial system in Eq.5 is possible; see App.5.

Appendix 5: Eq.3 can be reduced to $L_{no\ el\text{-}el} = 2\, \Sigma_{i=1}^{N/2} \Sigma_{k1=1}^{K} \Sigma_{k2=1}^{K} c_{i,k1}\, c_{i,k2} \int G_{k1}(1)\, h\, G_{k2}(1) d\mathbf{r_1} + \Sigma_{i=1}^{N/2} \Sigma_{j\geq i}^{N/2} \lambda_{ij}(\delta(i,j) - \Sigma_{k1=1}^{K} \Sigma_{k2=1}^{K} c_{i,k1}\, c_{j,k2} \int G_{k1}(1)\, G_{k2}(1) d\mathbf{r}_1)$ in the closed-shell case, for example. The Lagrange multipliers are also needed to obtain orthonormal solutions. The advantage is that this reduction device yields a third-order multivariable polynomial Lagrangian only, and Eq.5 reduces it to a second-order multivariable polynomial system only, containing only monomials c_{ik}, $c_{i1k1}c_{i2k2}$, and $\lambda_{i1j1}c_{i2k2}$ for ground and excited states. It yields good initial LCAO coefficients, which needs one more step to refine in finding the final (slightly different) LCAO coefficients; see App.6.

Appendix 6: Both ways to reduce the system (wherein no $1/r_{12}$ in the first step) in App.3 and App.5 must yield the same result for the first initial guesses for LCAO coefficients up to some small numerical error; algebraically, this is a polynomial system solver vs. an eigensolver problem, and their strong connection is well known.

Using the LCAO coefficients from $L_{no\ el\text{-}el}$ (App.4 and App.5) or from $\{y_k\}$ (App.3) for L in Eq.3 as initial values (the k^{th} solution is for the k^{th} excited state), the easy and fast standard multivariable Newton slope method moves the system into the corresponding minimum from its close vicinity. In more detail, this simple and effective algorithm finds a particular solution (depending on the initial value) iteratively for a multivariable nonlinear system (not necessarily only polynomial) as the polynomial system Eq.5: The gradient vector is $G(c_{ik}, \lambda_{ij}) = [\partial L/\partial c_{ik}, \partial L/\partial \lambda_{ij}]^T$ and the Jacobian of it is $J_G(c_{ik}, \lambda_{ij})$ in which, e.g., the first row is $[\partial^2 L/\partial {c_{11}}^2, \partial^2 L/(\partial c_{11}\partial c_{12}), \ldots, \partial^2 L/(\partial c_{11}\partial \lambda_{N/2,N/2})]$. In J_G, even more terms from L cancel systematically than in G by the second derivation. Finally, the optimal LCAO coefficients are obtained from Eq.7 in every step. One needs to repeat Eq.7 using all initial value sets in hand for $\{Y_k\}$.

Now, we have initial values (LCAO coefficient vectors) not only for the global minimum (ground state), but also for the lowest-lying excited states. All k cases converge to the corresponding and desired S_k one-determinant approximation located in the vicinity of initial values used; particularly, k = 0 converges to the ground state in Eq.1 and k > 0 for the lowest-lying excited states.

Appendix 7: The one-electron Hamiltonian matrix $\langle G_{k1}|h\, G_{k2}\rangle$ can be set up easily because it has one vector variable, $\mathbf{r}_1$. It yields close to MO spatial and energy eigenvalues. However, if operator H_{ee} is involved, then it becomes more complicated by the $1/r_{ij}$ terms; only the corresponding $\langle S_{k1}|H_{el}\, S_{k2}\rangle$ or $\langle Y_{k1}|H_{el}\, Y_{k2}\rangle$ can be set up afterward. In fact, it is the part of CI methods toward accurate (including correlation effect) solutions. (S_k can be calculated from an HF-SCF/basis pre-calculation using virtual orbitals as in the literature.) The diagonal element, $\langle S_k|H_{el}\, S_k\rangle$, provide

the one-determinant approximation for ground and excited states, detailed in this work using a direct, algebraic geometry way to determine S_k. This latter integral is based on the elementary relations $<\Psi_{k1}|H_{el}\ \Psi_{k2}> = E_{k2}\ \delta_{k1,k2}$ with $\Psi_k \approx S_k$.

Appendix 8: With the number of (singly and doubly) occupied MOs denoted by m, the following theorem holds: The Hamiltonian matrix $<G_{k1}|h\ G_{k2}>$ in Eq.6 using Eq.2 is diagonalized and the one-electron operator h (which reflects the nuclear frame of the system) yields (using, e.g., index i) eigenvectors $\{c_{i1}, c_{i2}, \ldots, c_{iK}\}$ and eigenvalues (MO energies) ε_i, ordered as $\varepsilon_{i-1} \leq \varepsilon_i$. (Basis set $\{G_k\}$ is orthonormalized.) For the reduced Lagrangian $L_{no\ el\text{-}el}(c_{ik}, c_{jk'}, \lambda_{ij}) = T + V_{ne} + \Sigma\lambda_{ij}(\delta(i,j) - \int i(1)j(1))$, the linear system $\{\partial L_{no\ el\text{-}el}/\partial c_{ik} = 0\}$ for λ_{ij} is solved, wherein i, j = 1, 2, 3, …m with $j \geq i$, k = 1, 2, …K, and importantly, all eigenvectors $\{c_{i1}, c_{i2}, \ldots, c_{iK}\}$ that were calculated are substituted into this linear system. It will yield $\lambda_{ij} = 0$ if $i \neq j$ and ε_i if i = j; the latter is $-\varepsilon_i$ if (scalar product −1) is written in Eq.3 instead of (1 - scalar product) in the conditions. This linear system has mK equations and m(m+1)/2 variables λ_{ij}, and $mK > m(m+1)/2$, so this linear system is overdetermined but not contradictory. Furthermore, some equations in the system are the trivial 0 = 0, which is to be dropped. This theorem also shows a close connection between the eigens (eigenvectors, eigenvalues) and the solution of the algebraic geometry problem in Eq.5.

Appendix 9: These basic two correlation energies are defined originally strictly for the k = 0 ground state for Eq.3 and Eq.9. Historically, the case in Eq.1 or Eq.3 occurred first. Through Eq.1, the correlation energy is $E_{corr}(HF, k) \equiv E_{k,el} - <S_k|H_{el}S_k>$ at optimized S_k, for which we know that $E_{corr}(HF, 0) < 0$ and variational. Through Eq.9, the $E_{corr}(DFT, k) \equiv E_{xc}(k) = E_x(k) + E_c(k)$, for which the exchange is $E_x(k) \equiv T - T(DFT)$, the correlation is $E_c(k) \equiv V_{ee} - V_{ee}(DFT)$, and we know that $E_x(0) > 0$, $E_c(0) < 0$, and $E_{xc}(0) < 0$ is non-variational. The $E_{corr}(HF, 0) \approx E_{corr}(DFT, 0)$, but not the same. Typically, $E_{corr}(HF, 0)$ is applied after HF calculation, while $E_{corr}(DFT, 0)$ is under (i.e., inserted in the KS-DFT algorithm). Our hypothesis is that $E_{corr}(HF, k) \approx E_{corr}(DFT, k) < 0$ and about 1%–2% of the electronic energy for the k^{th} excited states also, as for ground state k = 0. Other multiplicity cases (or spin states, that is, how many singly occupied MO are enforced) for closed and open shells are analogous to Eq.3 and Eq.9 and can be set up in straightforward ways; the difference is only in the number of terms in the summations (Σ_i^{m1} vs. Σ_i^{m2}).

We discuss the Lagrangians for any multiplicities in relation to DFT and discuss briefly the correlation energy, as shown in Eq.9. The new feature is that algebraic geometry can be applied to obtain the solutions, and excited states can also be obtained as in the HF approximations above; see the end of this appendix. We cannot review the extensive literature on the correlation energy here, we mention only that in Eq.9 and its other spin multiplicity cases for ground state (k = 0), the correlation effect is treated via the general functional $E_{corr}(DFT, 0) = \int\varepsilon[\rho_0(\mathbf{r}_1)]d\mathbf{r}_1$. The simplest integrands among the many suggested and tested ones with various characteristic names referring to which part of the correlation effect (kinetic, exchange, Coulombic, etc.) is taken into account, see for example, the emblematic expressions $\varepsilon[\rho_0(\mathbf{r}_1)] = \rho_0^{4/3}$ or $|\nabla\rho_0|^2/\rho_0$. Even spin dependencies are taken into account. The most common property of these in our algorithms is that these are nonlinear and non-polynomial [17–18]. In Eq.9, the one-electron T(DFT) + V_{ne} part yields second-order multivariable polynomials of LCAO coefficients, the Coulombic $V_{ee}(DFT)$ part yields fourth-order ones, while the $E_{corr}(DFT)$ term is non-polynomial in LCAO coefficients. However, the derivatives by the LCAO coefficients of the latter can be calculated for Eq.5 straightforwardly.

Our hypothesis is that the ground state literature established $E_{corr}(DFT, 0)$ formulas using ρ_0, which may be directly applied for $E_{corr}(DFT, k)$ with ρ_k, i.e., simply replacing the ρ_0 with ρ_k for excited states; $(\rho_k(\mathbf{r}_1) \equiv N\int S_k^* S_k ds_1 d\mathbf{x}_2 \ldots d\mathbf{x}_N$, where $\mathbf{x}_i$ are the spin-orbit coordinates). That is, simply the excited state one-electron density can be substituted to account for correlation effects in excited states, such as $\rho_k^{4/3}$ or $|\nabla\rho_k|^2/\rho_k$, etc.. However, we have not tested this hypothesis. Eq.9 and the other multiplicity cases can also be solved for LCAO coefficients with our algebraic geometry algorithms for Eq.5 to obtain ground and excited states as follow: Eq.9 without $E_{corr}(DFT, k)$ can be treated with algorithms 1, 2, and 3, for Eq.5, because this correlation-free Lagrangian is simply a polynomial of c_{ik}, while the full Eq.9 can be treated with algorithms 2 and 3 for Eq.5 because the derivatives $\partial E_{corr}(DFT, k)/\partial c_{ik}$ can be expressed and inserted in the Newton slope method in a straightforward way.

Additionally, if N = 2, then, with the Slater determinant in Eq.14, the $V_{ee}(HF) = \frac{1}{2}\int(f_1 g_2 - f_2 g_1)^2 r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$, while $\rho(i) = f_i^2 + g_i^2$ yields $V_{ee}(DFT) = \frac{1}{2}\int(f_1^2+g_1^2)(f_2^2+g_2^2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$, which is a different expression. $V_{ee}(DFT)$ does not contain the exchange integral. The shortcoming of the latter is that, for example, for an excited state neutral gas phase Li with naïve $1s(\alpha)2s(\alpha)2p_x(\alpha)$ vs. $1s(\alpha)2s(\alpha)2p_x(\beta)$ configurations, the $V_{ee}(HF)$ via Eq.4 distinguishes between the multiplicities with K_{ij}, but the $V_{ee}(DFT)$ does not. In DFT, the correlation term (via its operator) is added during SCF as in Eq.9. $V_{ee}(DFT)$ is also a fourth-order multivariable polynomial, as is the $V_{ee}(HF)$. Furthermore, $V_{ne}(HF) = V_{ne}(DFT) \equiv -\Sigma_{A=1}^{M} Z_A \int\rho_k(\mathbf{r}_1) R_{A1}^{-1} d\mathbf{r}_1$ is 100% accurate expression in the case of ground (k = 0) and excited (k > 0) states for any N; the only source of error comes from the inaccurate ρ_k.

Appendix 10: As a note to general CI methods, the addition of two N × M size matrices (A+B = C) is simple: Its $(i,j)^{th}$ element is simply $c_{ij} = a_{ij}+b_{ij}$. However, the analogous expression for two N × N size determinants is far more difficult, and the wave function is the sum of Slater determinants in the CI methods. The 1 × 1 case is the trivial det(A+B)= detA + detB, but for size 2 × 2, it is more complicated as det(A+B) = detA + detB + detA $Tr(A^{-1}B)$ = detA + detB + detB $Tr(B^{-1}A)$. For increasing size, N × N, the complexity of the expression increases very rapidly. In relation to wave functions, the number of electrons (N) is very large in practice (e.g., N = 68 for naphthalene), which is why manipulating them in this way is not tractable, so the approach what we are using is the general CI theory.

In the chapter on the helium correlation effect (section 6c), using the determinant basis set $\{Y_0, Y_1\}$ from App.3 for $\Psi_k \approx C_0Y_0 + C_1Y_1$, the CI Hamiltonian matrix is $[[<Y_0|H_{el}|Y_0>, <Y_1|H_{el}|Y_0>]^T, [<Y_0|H_{el}|Y_1>, <Y_1|H_{el}|Y_1>]^T] = [[e_0 + <f_1^2| 1/r_{12} |f_2^2|>, <f_1f_2| 1/r_{12} |g_1g_2>]^T, [<f_1f_2| 1/r_{12} |g_1g_2|>, e_1 + <g_1^2| 1/r_{12} |g_2^2>]^T]$, and analogously for N > 2 electron systems. Only two eigensolver steps are needed: The first is for Eq.6 to obtain the basis set $\{Y_0, Y_1\}$, and the second is for the CI Hamiltonian matrix via $\{Y_0, Y_1\}$ for (this simple) CI level ground and excited states. Converging the LCAO parameters with conventional SCF or with that in Eq.7 is not necessary at all. The orthonormal set $\{y_k\}$ and orthonormal set $\{Y_k\}$ are provided by the symmetric Hamiltonian matrices.

Conclusions

Some algorithms can replace the emblematic SCF part in HF-SCF and KS-DFT methods, these provide the ground and excited states with a one-determinant (HF) approximation. It is an improvement over the conventional literature SCF which is only for ground state primarily. Algorithm 1 is theoretically important, but we recommend algorithm 3 for practical calculations because it is fast and stable. Basically, the HF-SCF and KS-DFT methods are for ground states only; the excited states are calculated by different methods in the literature. However, algorithms 1–3 yield the lowest-lying excited states simultaneously and effectively. When we refer to excited states, we not only mean the lowest-lying (e.g., singlet/triplet Carbon atom excitations) but also the much higher ones.

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Abbreviations

AO = atomic orbital, approximated by, e.g,, STO-mG basis function (linear combination of Gaussian functions);
α_i, β_i = spin of electron i = 1,… N; $\delta(i,j)$ = Kronecker delta, 1 if i = j, and 0 if i ≠ j;
CI = Configuration interactions method;
DFT = Density Functional Theory method; DIIS = direct inversion in the iterative subspace method;
ee% = 100 $(E_{k,el} - E_{k,el,approx})/E_{k,el}$ = energy error in % for ground (k = 0) and k= 1, 2, 3, … excited states;
$E_{k,el}$, $E_{k,el}$(HF) = electronic energy of k^{th} excited state, $E_{k,el}$ on HF level approximation (see App.1);
$G_k(i) \equiv G_k(\mathbf{r}_i)$ = k^{th} basis function of $\mathbf{r}_i$ of electron i, e.g., STO-mG type is $G_k(i) = x_i^{n1}y_i^{n2}z_i^{n3} \exp(-a\,|\mathbf{r}_i-\mathbf{R}_A|^2)$;
h = one-electron operator in Eq.6, and also for unit hartree, not to be confused; (another is the Plank const.);
HF = Hartree-Fock method; H_{el} = non-relativistic Hamiltonian operator of the electronic energy; h = hartree;
KS-DFT = Kohn–Sham DFT;
L, L(HF) = Lagrangian, Lagrangian on HF level;
LCAO = linear combination of atomic orbitals; the coefficients in it, c_{ik}, are the k^{th} ones in the i^{th} spatial orbital;
m = mostly the number of (singly and doubly occupied) MOs in the molecular system;
M = number of atoms in the molecular system;
MO = molecular orbital; their spatial part is notated as $f_1 = f(\mathbf{r}_1)$, $g_1 = g(\mathbf{r}_1)$, or $i(1) = f(\mathbf{r}_1)$, $j(2) = g(\mathbf{r}_2)$ etc.;
N = number of electrons in the system;
$\mathbf{r}_i$ = position vector of electron i in Cartesian coordinates, i = 1, 2, … N;
$\mathbf{R}_A = (R_{Ax}, R_{Ay}, R_{Az})$ = position vector of nucleus of atom A = 1, 2, …M; component R_{Au} with u = x, y, z;
SCF = self-consistent field method; ROHF = restricted open-shell HF; UHF = unrestricted HF;
Spin multiplicity ≡ $S = 1 + 2\,\Sigma_{i=1}^{N} s_i$, where s_i is the i^{th} electron spin, ½ for α and –½ for β;
STO = Slater type orbitals, $x_i^{n1}y_i^{n2}z_i^{n3} \exp(-a\,|\mathbf{r}_i-\mathbf{R}_A|)$, where a = Z/n in the case of Hydrogen-like atoms; see ref.[7];
STO-mG = Hydrogen-like atomic wave functions are approximated with m LC of Gaussians to create basis sets;
T, V_{ne}, V_{ee}, V_{nn} = kinetic, nuclear-electron attr., electron-electron rep., nuclear-nuclear rep. energy of the system;

Z_A = atomic charge (atomic number) of atom A = 1, 2, …M;
$\langle f|g\rangle \equiv \int (f^* g)d\mathbf{r}$ and $\langle f|r_{12}^{-1}|g\rangle \equiv \int (f^* r_{12}^{-1} g)d\mathbf{r}_1 d\mathbf{r}_2$, the integration is over the full 3D and 6D spatial spaces, resp.,
f* = f for real functions in relations to complex conjugates.

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