Effective local potentials for excited states

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The constrained variational Hartree–Fock method for excited states of the same symmetry as the ground state [Chem. Phys. Lett. 287, 189 (1998)] is combined with the effective local potential (ELP) method [J. Chem. Phys. 125, 081104 (2006)] to generate Kohn–Sham-type exact-exchange potentials for singly excited states of many-electron systems. Illustrative examples include the three lowest $^2S$ states of the Li and Na atoms and the three lowest $^3S$ states of He and Be. For the systems studied, excited-state ELPs differ from the corresponding ground-state potentials in two respects: They are less negative and have small additional “bumps” in the outer electron region. The technique is general and can be used to approximate excited-state exchange-correlation potentials for other orbital-dependent functionals. © 2010 American Institute of Physics. [doi:10.1063/1.3521492]

I. INTRODUCTION

One of the outstanding problems in modern density-functional theory (DFT) is accurate and efficient construction of multiplicative (local) Kohn–Sham potentials for orbital-dependent exchange-correlation functionals. Such potentials are desired because they lead to better results in calculations of molecular response properties than the corresponding nonlocal potentials obtained as functional derivatives with respect to orbitals (see Refs. 4–10, and 11 and references therein).

Consider the exact expression for the density-functional exchange energy

\[ E_X = -\frac{1}{2} \sum_{\sigma} \sum_{i,j=1}^{N^\sigma} \int d\mathbf{r} \int d\mathbf{r}' \frac{\phi_i^\sigma(\mathbf{r}) \phi_j^\sigma(\mathbf{r}') \phi_j^\sigma(\mathbf{r}) \phi_i^\sigma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \]

(1)

where $\phi_i^\sigma$ are Kohn–Sham orbitals and $N^\sigma$ is the number of $\sigma$-spin electrons ($\sigma = \alpha, \beta$). The corresponding Kohn–Sham potential, defined as $V_X^\sigma(\mathbf{r}) = -\delta E_X/\delta \rho_\sigma$, cannot be evaluated simply by taking the functional derivative of $E_X$ with respect to $\rho_\sigma$ because $E_X$ cannot be written as an explicit functional of the density. In such cases, the functional derivative $V_X^\sigma(\mathbf{r})$ has to be found indirectly. This can be done, for instance, by solving the optimized effective potential (OEP) equation\(^1\)-\(^3\) which relates $V_X^\sigma(\mathbf{r})$ to readily available functional derivatives of the type $\delta E_X/\delta \phi_i^\sigma$.

Most practical methods for solving the OEP equation introduce an orbital basis set to represent the Kohn–Sham orbitals and an auxiliary basis set to expand the potential $V_X^\sigma(\mathbf{r})$.\(^1\)-\(^5\) Accumulated experience with finite-basis-set OEP implementations demonstrated that, in order to obtain sensible results, one has to maintain a delicate balance between the orbital and auxiliary basis sets.\(^1\)-\(^5\) Nevertheless, inherent numerical difficulties of the exact-exchange-only OEP technique continue to offset its advantages over nonlocal-potential methods in calculations of static response properties. It has been even argued that “any apparent improvement of the exact-exchange OEP method over the Hartree–Fock scheme for a finite fit basis set must be considered spurious.”\(^26\)

An alternative to solving the OEP equation is the effective local potential (ELP) method.\(^27\)-\(^29\) In this approach, the functional derivative of $E_X$ is approximated by the local potential $\hat{V}_X^\sigma(\mathbf{r})$ that minimizes the variance of the difference between $V_X^\sigma(\mathbf{r})$ and its nonlocal counterpart,

\[ \hat{V}_X^\sigma(\mathbf{r}) \equiv \frac{\delta E_X[|\phi_j^\sigma(\mathbf{r})|]}{\delta \phi_j^\sigma(\mathbf{r})} = - \sum_j^{N^\sigma} \hat{K}_j^\sigma \phi_j^\sigma(\mathbf{r}), \]

(2)

in which $\hat{K}_j^\sigma$ is the conventional one-electron exchange operator of the Hartree–Fock theory,

\[ \hat{K}_j^\sigma \phi_j^\sigma(\mathbf{r}) = \int d\mathbf{r}' \frac{\phi_j^\sigma(\mathbf{r}') \phi_j^\sigma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_j^\sigma(\mathbf{r}). \]

(3)

This makes an ELP the best local approximation to $\hat{V}_X^\sigma$ in the least squares sense. To a good accuracy, the Kohn–Sham orbitals $\phi_j^\sigma$ in the ELP procedure may be replaced with converged and fixed Hartree–Fock orbitals.\(^27\) In this case, the ELP problem has an explicit analytic solution which is closely related\(^28\),\(^30\) to the localized Hartree–Fock\(^4\) (LHF) and common-energy-denominator\(^31\) (CEDA) approximations to the OEP.

ELPs derived from Hartree–Fock orbitals are known to be good approximations to the exact exchange OEP for ground states.\(^27\),\(^32\) From the practical point of view, the most attractive feature of ELPs is that they are more stable with respect to imbalances in the orbital and auxiliary basis sets than finite-basis-set solutions of the OEP equation.\(^27\) Another advantage of exchange ELPs is that they can be easily constructed in any situation where Hartree–Fock orbitals are available.

Extension of time-independent (static) DFT to excited states of the same symmetry as the ground state is neither
Section III presents illustrative examples.

II. METHODOLOGY

The central idea of the ELP method for excited states is to obtain an excited-state Hartree–Fock–Fock SCF wave function in an orbital basis set and then generate the corresponding ELP using an auxiliary basis set. After that, one can solve the Kohn–Sham equations to obtain an estimate of the excited-state Kohn–Sham energy. Details of this procedure are presented below. To distinguish between Hartree–Fock and Kohn–Sham determinants, we will use the notation $\psi_\sigma$ and $\phi_\alpha$ for the former and $\phi_\beta$ for the latter. Kohn–Sham and Hartree–Fock determinants will be denoted $\Phi$ and $\Psi$, respectively.

A. Unrestricted and restricted self-consistent-field methods for excited states

Let us first recall how the unrestricted Hartree–Fock (UHF) SCF method\(^{40}\) is applied to the ground state of an open-shell high-spin system with $N^\alpha$ spin-up and $N^\beta$ spin-down electrons. Without loss of generality, we assume that $N^\alpha \geq N^\beta$. Given an unrestricted Slater determinant $\Psi$ constructed with spatial orbitals $\psi_\alpha$ and $\psi_\beta$ and spin functions $\alpha$ and $\beta$, the total electronic energy of the system is an orbital functional given by

$$E_{\text{tot}}[\psi_\alpha^\sigma] = \sum_{\sigma} \sum_{i=1}^{N^\sigma} \langle \psi_\alpha^\sigma | -\frac{1}{2} \nabla^2 | \psi_\alpha^\sigma \rangle + \int \rho(r) v_{\text{ext}}(r) \, dr + \frac{1}{2} \int \rho(r) v_J(r) \, dr + E_X[\psi_\alpha^\sigma],$$

where $v_{\text{ext}}(r)$ is the external potential, $v_J(r)$ is the Coulomb potential, and $E_X$ is given by Eq. (1) with $\psi_\alpha^\sigma$ in lieu of $\phi_\alpha$. To derive the UHF equations for the ground state we minimize $E_{\text{tot}}$ with respect to orbitals $\psi_\alpha^\sigma$, subject to the constraint $\langle \psi_\alpha^\sigma | \psi_\alpha^\sigma \rangle = \delta_{ij}$. That is, we replace the constrained minimization of $E_{\text{tot}}$ with unconstrained minimization of the functional

$$L_{\text{UHF}} = E_{\text{tot}} + \sum_{\sigma} \sum_{i,j=1}^{N^\sigma} \epsilon_{ij}^\sigma (\delta_{ij} - \langle \psi_\alpha^\sigma | \psi_\alpha^\sigma \rangle),$$

where $\epsilon_{ij}^\sigma$ are Lagrange multipliers. Recall that there exists\(^{40}\) a set of orbitals $\psi_\alpha^\sigma$ for which the matrix of the Lagrange multipliers is diagonal, i.e., $\epsilon_{ij}^\sigma = \epsilon_i^\sigma \delta_{ij}$. In terms of these orbitals, the condition that $L_{\text{UHF}}$ is stationary has the form of the canonical UHF equations

$$\hat{f}^\sigma \psi_i^\sigma = \epsilon_i^\sigma \psi_i^\sigma,$$

where

$$\hat{f}^\sigma = -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r) + v_J(r) + \hat{V}_X^\sigma.$$

Here $\hat{V}_X^\sigma$ is given by Eq. (2) with $\psi_\alpha^\sigma$ in place of $\phi_\alpha^\sigma$.

The restricted open-shell Hartree–Fock (ROHF) method differs from UHF in one respect, namely, by the requirement that the Hartree–Fock wave function $\Psi$ be also an eigenfunction of $S^2$. As shown by Fock,\(^{41}\) this condition is fulfilled if the occupied $\beta$-spin orbitals are linear combinations of the occupied $\alpha$-spin orbitals. This allows one to cast the requirement that $\Psi$ be a spin eigenfunction as the constraint\(^{42}\)

$$\sum_{i=1}^{N^\beta} \langle \psi_\beta^\alpha | \hat{Q}^\alpha | \psi_\beta^\alpha \rangle = 0,$$

where $\hat{Q}^\alpha$ is the projector onto the subspace of the $\alpha$-spin virtual orbitals, that is,

$$\hat{Q}^\alpha = \hat{I} - \hat{P}^\alpha,$$

in which $\hat{I}$ is the identity operator and

$$\hat{P}^\alpha \equiv \sum_{i=1}^{N^\alpha} | \psi_i^\alpha \rangle \langle \psi_i^\alpha |$$

is the projector onto the subspace of the occupied $\alpha$-spin orbitals. Thus, the ROHF solution can be obtained by an unconstrained minimization of the functional

$$L_{\text{ROHF}} = L_{\text{UHF}} + \lambda_S \sum_{i=1}^{N^\beta} \langle \psi_i^\beta | \hat{Q}^\alpha | \psi_i^\beta \rangle,$$

where $\lambda_S$ is a Lagrange multiplier. Using the above expression for $\hat{Q}^\alpha$, it is straightforward to show\(^{42}\) that the condition for an extremum of $L_{\text{ROHF}}$ with respect to variations of orbitals $\psi_i^\beta$ leads to the equations

$$(\hat{f}^\beta - \lambda_S \hat{P}^\beta) \psi_i^\beta = \epsilon_i^\beta \psi_i^\beta,$$

$$(\hat{f}^\beta + \lambda_S \hat{Q}^\alpha) \psi_i^\beta = \epsilon_i^\beta \psi_i^\beta,$$

where $\hat{f}^\beta$ and $\hat{f}^\beta$ are the conventional Fock operators of Eq. (7) and $\hat{P}^\beta = \sum_{i=1}^{N^\beta} | \psi_i^\beta \rangle \langle \psi_i^\beta |$. The ROHF solution of Eqs. (12) and (13) is obtained in the limit $\lambda_S \to \infty$\(^{37,38,43}\). For high-spin states, this yields the same spin-restricted determinants as Roothaan’s coupling-operator method.\(^{44}\) The above formulation of the ROHF procedure is closely related to that of Andrews et al.\(^{45}\)

Various extensions of the Hartree–Fock SCF scheme to excited states have been proposed in the literature.\(^{46–53}\) One particularly convenient adaptation of the Hartree–Fock method to excited states was suggested by Glushkov in Ref. 34 and elaborated in Refs. 35–38, and 39. We will now review this method and present it, for the first time, in the form of readily programmable matrix equations.
Suppose we want to obtain the best one-determinantal approximation \( \Psi_1 \) for the first excited state of the system. The determinant \( \Psi_1 \) is to be constructed with excited-state orbitals \( \psi_1^\alpha \). Suppose also that we have already obtained a UHF or an ROHF determinant \( \Psi_0 \) for the ground state of the same system. This determinant is built with orbitals \( \psi_i^\alpha \). To keep our notation simple, here and below we use state-number subscripts only for orbitals of the lower-lying states, but omit them for orbitals of the target (highest) state.

To obtain the excited-state determinant \( \Psi_1 \) we assume that \( \Psi_1 \) is orthogonal to \( \Psi_0 \) and impose the requirement \( \langle \Psi_1 | \Psi_0 \rangle = 0 \) as a constraint in the variational procedure. The assumption of orthogonality of SCF wave functions is legitimate for high-spin states studied in this work, although it alone does not guarantee that \( \Psi_1 \) gives an upper bound to the exact first excited-state energy and may not be appropriate in other situations such as open-shell singlets.

As shown in Sec. 3.2 of Ref. 38, if we consider single excitations from the \( \alpha \)-spin highest occupied molecular orbital (HOMO) of \( \Psi_0 \), \( \psi_{\text{HOMO},0}^\alpha \), then \( \Psi_1 \) will be orthogonal to \( \Psi_0 \) if all \( \alpha \)-orbitals of \( \Psi_1 \) are orthogonal to \( \psi_{\text{HOMO},0}^\alpha \). Thus, the condition \( \langle \Psi_1 | \Psi_0 \rangle = 0 \) is equivalent to

\[
\sum_{i=1}^{N^\alpha} \langle \psi_i^\alpha | \hat{P}_{\text{HOMO},0}^\alpha | \psi_i^\alpha \rangle = 0, \quad (14)
\]

where

\[
\hat{P}_{\text{HOMO},0}^\alpha = | \psi_{\text{HOMO},0}^\alpha \rangle \langle \psi_{\text{HOMO},0}^\alpha | \quad (15)
\]

is the projector onto the subspace defined by \( \psi_{\text{HOMO},0}^\alpha \). The orbitals \( \psi_i^\alpha \) and \( \psi_i^\beta \) can now be obtained by the variation method as the orbitals that minimize the functional \( L_{\text{UHF}} \) (or \( L_{\text{ROHF}} \)), subject to the constraint of Eq. (14). Introducing another Lagrange multiplier, \( \lambda_O \), we reformulate the variational search for the first excited-state UHF determinant \( \Psi_1 \) as an unconstrained minimization of the functional

\[
L_{\text{UHF}}^{(1)} = L_{\text{UHF}} + \lambda_O \sum_{i=1}^{N^\alpha} \langle \psi_i^\alpha | \hat{P}_{\text{HOMO},0}^\alpha | \psi_i^\alpha \rangle, \quad (16)
\]

where \( L_{\text{UHF}} \) is given by Eq. (5). If we also want \( \Psi_1 \) to be an eigenfunction of \( \hat{S}^2 \), we minimize the functional

\[
L_{\text{ROHF}}^{(1)} = L_{\text{UHF}}^{(1)} + \lambda_S \sum_{i=1}^{N^\beta} \langle \psi_i^\beta | \hat{Q}_{\text{HOMO},0}^\beta | \psi_i^\beta \rangle, \quad (17)
\]

If we want to obtain an ROHF determinant for the \( n \)-th excited state, we require it to be orthogonal to all the lower-lying determinants, \( \langle \psi_n | \psi_k \rangle = 0 \), where \( k = 0, 1, 2, \ldots, n - 1 \). Accordingly, the functional \( L_{\text{ROHF}}^{(1)} \) should be replaced for the \( n \)-th state with

\[
L_{\text{ROHF}}^{(n)} = L_{\text{UHF}} + \lambda_S \sum_{i=1}^{N^\beta} \langle \psi_i^\beta | \hat{Q}_{\text{HOMO},0}^\beta | \psi_i^\beta \rangle + \lambda_O \sum_{i=1}^{N^\alpha} \langle \psi_i^\alpha | \hat{P}_{\text{HOMO},0}^\alpha | \psi_i^\alpha \rangle, \quad (18)
\]

where

\[
\hat{P}_{\text{HOMO},0}^\alpha = | \psi_{\text{HOMO},0}^\alpha \rangle \langle \psi_{\text{HOMO},0}^\alpha | \quad (19)
\]

is the projector onto the space defined by the \( \alpha \)-spin HOMO of the \( k \)-th state.

It is easy to see that the condition for an extremum of the excited-state ROHF functional, \( \delta L_{\text{ROHF}}^{(n)} = 0 \), reduces to the following set of eigenvalue problems

\[
\left( \hat{P}_n^\beta - \lambda_S \hat{P}_n^\alpha + \lambda_O \sum_{k=0}^{n-1} \hat{P}_{\text{HOMO},k}^\alpha \right) \psi_i^\alpha = \epsilon_i^\alpha \psi_i^\alpha, \quad (20)
\]

\[
(\hat{P}_n^\alpha + \lambda_S \hat{Q}_{\text{HOMO},0}^\alpha) \psi_i^\beta = \epsilon_i^\beta \psi_i^\beta. \quad (21)
\]

Equations (20) and (21) represent the constrained variational SCF method in its general form. The orthogonality constraint of Eq. (14) is satisfied in the limit \( \lambda_O \rightarrow \infty \). By setting \( \lambda_S = 0 \) we can relax the spin-purity constraint and go back from ROHF to UHF solutions. By setting \( \lambda_O = 0 \), we fall back to the ground state.

In practice, Eqs. (20) and (21) are solved by expanding the orbitals in a finite set of real basis functions,

\[
\psi_i^\alpha (\mathbf{r}) = \sum_{\mu=1}^{M_{\text{orb}}} c_{\mu,i} \chi_\mu (\mathbf{r}), \quad (22)
\]

For simplicity, let us assume here that the same orbital basis set \( \{ \chi_\mu \} \) is used for the desired \( n \)-th state and for all the lower-lying states. The general case of different basis sets for different states requires a minor modification which will be dealt with at the end of this section.

Once the basis set \( \{ \chi_\mu \} \) is introduced, the integro-differential Eqs. (20) and (21) become generalized matrix eigenvalue problems:

\[
\tilde{F}^\alpha c_i^\alpha = \epsilon_i^\alpha S^\alpha c_i^\alpha, \quad (23)
\]

where \( \epsilon_i^\alpha \) are column-vectors of the coefficients \( c_{\mu,i}^\alpha \), \( S \) is an overlap matrix with the elements

\[
S_{\mu \nu} = \langle \chi_\mu | \chi_\nu \rangle, \quad (24)
\]

and \( \tilde{F}^\alpha \) are modified Fock matrices given by

\[
\tilde{F}^\alpha = F^\alpha - \lambda_S S^\alpha P^\beta S + \lambda_O \sum_{k=0}^{n-1} S^\alpha P_{\text{HOMO},k}^\alpha S \quad (25)
\]

\[
\tilde{F}^\beta = F^\beta + \lambda_S S^\alpha Q^\alpha S \quad (26)
\]

Here \( F^\alpha \) and \( F^\beta \) are the standard Fock matrices with the elements \( F_{\mu \nu}^{\alpha} = \langle \chi_\mu | \hat{F}^{\alpha} | \chi_\nu \rangle \), \( P^\beta \) is the \( \beta \)-spin density matrix

\[
P^\beta = \sum_{i=1}^{N^\beta} c_i^\beta (c_i^\beta)^T, \quad (27)
\]

\( Q^\alpha \) is the \( \alpha \)-spin virtual density matrix,

\[
Q^\alpha = \sum_{j=N^\alpha+1}^{M_{\text{orb}}} c_j^\alpha (c_j^\alpha)^T, \quad (28)
\]

and \( P_{\text{HOMO},k}^\alpha \) is given by

\[
P_{\text{HOMO},k}^\alpha = c_{\text{HOMO},k}^\alpha (c_{\text{HOMO},k}^\alpha)^T, \quad (29)
\]

where \( c_{\text{HOMO},k}^\alpha \) is a column-vector of molecular orbital coefficients for \( \psi_{\text{HOMO},k}^\alpha \). As Eq. (28) implies, we replace the identity operator in Eq. (9) by its finite-basis set representation.
\[ I = \sum_{i=1}^{M_{\text{orb}}} |\psi_i\rangle\langle \psi_i|, \]

where \( M_{\text{orb}} \) is the total number of (occupied and virtual) Hartree–Fock orbitals. Normally, \( M_{\text{orb}} \) is equal to \( M_{\text{bas}} \), the total number of basis functions in Eq. (22).

Since neither \( \lambda_S \) nor \( \lambda_O \) can be infinity in practical calculations, one has to settle on some large finite values. On the one hand, the greater the value of \( \lambda_S \) or \( \lambda_O \), the more accurately the respective constraint is satisfied. On the other hand, large values of \( \lambda_S \) and \( \lambda_O \) make it more difficult to converge the SCF procedure. Reasonable compromise is achieved when both \( \lambda_S \) and \( \lambda_O \) are of the order of \( 10^2 \)–\( 10^3 \) hartrees \((E_h)\).\(^{37,38}\)

The recommended values employed throughout this work are \( \lambda_S = 100 \) \( E_h \) for the spin-purity constraint and \( \lambda_O = 1000 \) \( E_h \) for the orthogonality constraint.

B. ELP method for excited states

In the exchange-only Kohn–Sham scheme for ground states, the total energy functional has the form of Eq. (4) with \( \psi_i^0 \) replaced by \( \phi_i^0 \). This function is minimized with respect to \( \phi_i^0 \), subject to the constraints that these orbitals be orthonormal and that they be eigenfunctions of an effective one-electron Hamiltonian. This Hamiltonian turns out to have the form

\[ \hat{H}^0 = -\frac{1}{2} \nabla^2 + v_{\text{ex}}(\mathbf{r}) + v_J(\mathbf{r}) + v_{\text{v}}(\mathbf{r}), \]

where \( v_{\text{v}}(\mathbf{r}) \) is obtained as the functional derivative of \( E_X[(\phi_i^0)] \) with respect to \( \rho_0(\mathbf{r}) \). The condition for an extremum of \( E_{\text{tot}}[(\phi_i^0)] \) is the Kohn–Sham equations,

\[ \hat{H}^0 \phi_i^0 = \epsilon_i^0 \phi_i^0. \]

A Slater determinant constructed with the solutions \( \phi_i^0 \) is referred to as a Kohn–Sham determinant.

The ELP method is a version of the above scheme in which \( v_{\text{v}}(\mathbf{r}) \) is obtained by minimizing the quantity \( S^0 \), the variance of \( v_X^0 - \hat{V}^0(\mathbf{r}) \) constructed and evaluated using fixed Hartree–Fock orbitals \( \psi_i^0 \). To find this potential, we follow Ref. 27 and expand \( v_X^0 \) in a set of auxiliary basis functions,

\[ v_{\text{v}}^0(\mathbf{r}) = \sum_{m=1}^{M_{\text{aux}}} b_m^0 g_m(\mathbf{r}), \]

and then determine the coefficients \( \{b_m^0\} \) by solving the system of equations

\[ \delta S^0 / \delta b_m^0 = 0. \]

As shown in Ref. 27, this task reduces to solving the matrix equation

\[ A^0 b^0 = d^0, \]

where

\[ A_{\mu\nu}^0 = \sum_{i=1}^{N_e} \langle \psi_i^0 | \hat{g}_m | \psi_i^0 \rangle - \sum_{i,j=1}^{N_e} \langle \psi_i^0 | \hat{g}_m | \psi_j^0 \rangle \langle \psi_j^0 | g_i | \psi_i^0 \rangle, \]

and

\[ d_{\mu}^0 = \sum_{i=1}^{N_e} \langle \psi_i^0 | \hat{V}^0_X | \psi_i^0 \rangle - \sum_{i,j=1}^{N_e} \langle \psi_i^0 | \hat{V}^0_X | \psi_j^0 \rangle \langle \psi_j^0 | \hat{V}^0_X | \psi_i^0 \rangle. \]

Once the potential \( v_{\text{v}}^0(\mathbf{r}) \) is generated, it is held fixed and Eq. (31) is solved self-consistently. (This is needed because \( \hat{H}^0 \) still depends on \( \phi_i^0 \) through \( v_{\text{v}} \).)

Excited-state ELPs can be obtained directly from the converged Hartree–Fock orbitals of the corresponding excited state by solving Eq. (33). However, if we wish to use an excited-state ELP to solve the Kohn–Sham equations, the Kohn–Sham Hamiltonian of Eq. (30) must be somehow modified to prevent variational collapse. To this end, we require that each excited-state Kohn–Sham determinant be orthogonal to the Hartree–Fock determinant of every lower-lying state, that is, we require that \( \langle \Phi_n | \Psi_k \rangle = 0 \), where \( k = 0, 1, 2, \ldots, n - 1 \). The rationale for this choice is given at the end of this section.

By analogy with the excited-state Hartree–Fock method, the constraints \( \langle \Phi_n | \Psi_k \rangle = 0 \) are imposed via Lagrange multipliers. Using arguments similar to those leading to Eqs. (20) and (21), we arrive at the spin-restricted exchange-only Kohn–Sham equations for the \( n \)th excited state:

\[ \left( \hat{H}^0 - \lambda_S \hat{P}^0_{\text{KS}} + \lambda_O \sum_{k=0}^{n-1} \hat{P}^\alpha_{\text{HOMO},k} \right) \phi_i^\alpha = \epsilon_i^\alpha \phi_i^\alpha, \]

\[ \left( \hat{H}^0 + \lambda_S \hat{Q}^0_{\text{KS}} \right) \phi_i^\beta = \epsilon_i^\beta \phi_i^\beta, \]

where \( \hat{P}^\alpha_{\text{HOMO},k} \) is the projector onto the space of the Hartree–Fock HOMO of the \( k \)th state, \( \hat{P}^0_{\text{KS}} = \sum_{i=1}^{N^0} |\phi_i^0 \rangle \langle \phi_i^0| \) is the projector onto the space of the occupied \( \beta \)-spin Kohn–Sham orbitals, and \( \hat{Q}^0_{\text{KS}} = \hat{I} - \hat{P}^0_{\text{KS}} \) is the projector onto the space of the virtual \( \alpha \)-spin Kohn–Sham orbitals.

Introducing as before a finite one-electron basis set \( \{ \chi_{\mu} \} \) we expand the Kohn–Sham orbitals,

\[ \phi_i^\alpha(\mathbf{r}) = \sum_{\mu=1}^{M_{\text{bas}}} a_{\mu\alpha}^i \chi_\mu(\mathbf{r}), \]

and write Eqs. (36) and (37) in matrix form

\[ \hat{H}^0 a_i^\alpha = \epsilon_i^\alpha S a_i^\alpha, \]

where

\[ \hat{H}^0 = H^0 - \lambda_S S P^0_{\text{KS}} + \lambda_O \sum_{k=0}^{n-1} S P^\alpha_{\text{HOMO},k}, \]

\[ \hat{H}^\beta = H^\beta + \lambda_S S Q^0_{\text{KS}}. \]

Here \( H^\alpha \) and \( H^\beta \) are the standard Kohn–Sham matrices with the elements \( H^\mu_{\nu} = \langle \chi_{\mu} | \hat{H}^0 | \chi_{\nu} \rangle \), \( S \) is the overlap matrix for the basis set \( \{ \chi_{\mu} \} \), and \( P^\alpha_{\text{HOMO},k} \) is given by Eq. (29), \( P^\alpha_{\text{KS}} = \sum_{\mu,i,j=1}^{M_{\text{bas}}} a_{\mu\alpha}^i a_{\mu\alpha}^j \), and \( Q^0_{\text{KS}} = \sum_{j=1}^{M_{\text{bas}}} a_{j\beta}^i a_{j\beta}^j \). The modified Kohn–Sham Eq. (39) is solved self-consistently in the same manner as the excited-state Hartree–Fock equations.

Let us now summarize our method. Suppose we want to perform an ELP calculation for the \( n \)th excited state of a given symmetry. The algorithm is as follows.

1. Solve the modified Hartree–Fock Eq. (23) for the lowest state and excited states 1 through \( n \).
2. Using the Hartree–Fock orbitals for the nth excited state, obtain the ELP by solving Eq. (33).
3. Construct the matrices of Eqs. (40) and (41) and solve the Kohn–Sham Eq. (39).
4. Using the Kohn–Sham orbitals obtained in step 3, evaluate the total energy $E_{\text{tot}}[\{\phi_k^e\}]$.

There are at least two reasons why our orthogonality constraint pegs Kohn–Sham determinants to Hartree–Fock determinants rather than to other Kohn–Sham determinants. First, mutual orthogonality is a property of interacting wave functions of the ground and excited states, not of the corresponding Kohn–Sham determinants. Second, the ELP energy for ground states is always above the corresponding Hartree–Fock determinations. Second, the ELP energy for excited states is always above the corresponding Hartree–Fock determinations.

C. Different basis sets for different states

Generally, it is desirable to use different orbital basis sets for different states. This is because calculations on excited states can be meaningless without including sufficiently diffuse basis functions, whereas for ground states such functions may not be needed at all. Suppose we use an orbital basis set $\{\chi_k\}$ for the target nth excited state and a state-specific basis set $\{\chi_k^e\}$ for each lower-lying state $k (k = 0, 1, 2, \ldots, n - 1)$. In the context of the excited-state Hartree–Fock and ELP methods, this requires a small modification of our working equations. Specifically, the last term in Eqs. (25) and (40) must be replaced with

$$
\lambda_c \sum_{k=0}^{n-1} S_k^2 P_{\text{HOMO}, \lambda} S_k,
$$

where $S_k$ is a matrix with the elements

$$
(S_k)_{\mu\nu} = \langle \chi_k^e | \chi_{\nu} \rangle.
$$

Generally, matrices $S_k$ are rectangular. However, if the basis sets $\{\chi_k\}$ and $\{\chi_k^e\}$ are chosen to be identical, then $S_k = S$ (square).

Overlap matrices $S_k$ may not be readily available in standard SCF codes. In such cases, one can use the same basis set for all states of interest, from the lowest to the highest. Of course, such a basis set has to be very flexible (that is, contain sufficiently many diffuse functions) and would be oversaturated for low-lying states.

III. NUMERICAL CALCULATIONS

The excited-state Hartree–Fock and excited-state ELP methods described in the previous section were implemented in a development version of the GAUSSIAN program. This section presents results of numerical calculations carried out with this implementation.

A. Basis sets for orbitals and potentials

For each system studied in this work, we opted to use one common orbital basis set and one common auxiliary basis set for all target states. Since standard basis sets are not suited for this purpose, we developed customized even-tempered sets of primitive Gaussian-type functions, both for Kohn–Sham orbitals and for ELPs. The exponents of these functions are obtained by the prescription

$$
\xi_m = \zeta_0 \gamma^{m-1}, \quad m = 1, 2, \ldots, M,
$$

where the values of parameters $M$, $\zeta_0$, and $\gamma$ are given in Table I. These values were chosen after extensive experimentation with Schmidt–Ruedenberg sequences augmented with a few diffuse functions, but otherwise they were not optimized. Observe that the smallest exponents $\zeta_0$ in our orbital (and even auxiliary) basis sets are much smaller than in standard basis sets. Note also that the number of auxiliary basis functions is generally smaller than the number of orbital basis functions. This is because very tight functions ($\xi_m > 10^3$) are needed for orbital expansions but not for potentials.

While developing auxiliary basis sets we observed that very diffuse functions may cause the matrix $A$ of Eq. (33) to become ill-conditioned. We monitored the matrix $A$ for effective rank-deficiency by using the LAPACK subroutine

<table>
<thead>
<tr>
<th>Atom</th>
<th>Basis</th>
<th>Specification</th>
<th>$\zeta_0$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>orb-S</td>
<td>(8s)</td>
<td>0.00486</td>
<td>3.59</td>
</tr>
<tr>
<td></td>
<td>orb-M</td>
<td>(15s)</td>
<td>0.00324</td>
<td>2.54</td>
</tr>
<tr>
<td></td>
<td>orb-L</td>
<td>(22s)</td>
<td>0.00216</td>
<td>2.17</td>
</tr>
<tr>
<td>Li</td>
<td>orb-S</td>
<td>(9s)</td>
<td>0.00407</td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td>orb-M</td>
<td>(15s)</td>
<td>0.00240</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>orb-L</td>
<td>(22s)</td>
<td>0.00141</td>
<td>2.24</td>
</tr>
<tr>
<td>Be</td>
<td>orb-S</td>
<td>(8s)</td>
<td>0.00364</td>
<td>3.98</td>
</tr>
<tr>
<td></td>
<td>orb-M</td>
<td>(15s)</td>
<td>0.00273</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>orb-L</td>
<td>(22s)</td>
<td>0.00182</td>
<td>2.30</td>
</tr>
<tr>
<td>Na</td>
<td>orb-S</td>
<td>(10s4p)</td>
<td>0.000151, 0.673a</td>
<td>3.96</td>
</tr>
<tr>
<td></td>
<td>orb-M</td>
<td>(16s7p)</td>
<td>0.00101, 0.360a</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>orb-L</td>
<td>(24s10p)</td>
<td>0.00067, 0.256a</td>
<td>2.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Basis</th>
<th>Specification</th>
<th>$\zeta_0$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>aux-S</td>
<td>(6s)</td>
<td>0.036</td>
<td>3.59</td>
</tr>
<tr>
<td></td>
<td>aux-M</td>
<td>(10s)</td>
<td>0.024</td>
<td>2.54</td>
</tr>
<tr>
<td></td>
<td>aux-L</td>
<td>(16s)</td>
<td>0.016</td>
<td>2.17</td>
</tr>
<tr>
<td>Li</td>
<td>aux-S</td>
<td>(6s)</td>
<td>0.028</td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td>aux-M</td>
<td>(10s)</td>
<td>0.020</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>aux-L</td>
<td>(16s)</td>
<td>0.014</td>
<td>2.24</td>
</tr>
<tr>
<td>Be</td>
<td>aux-S</td>
<td>(6s)</td>
<td>0.030</td>
<td>4.45</td>
</tr>
<tr>
<td></td>
<td>aux-M</td>
<td>(9s)</td>
<td>0.025</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>aux-L</td>
<td>(12s)</td>
<td>0.020</td>
<td>2.30</td>
</tr>
<tr>
<td>Na</td>
<td>aux-S</td>
<td>(6s)</td>
<td>0.075</td>
<td>3.96</td>
</tr>
<tr>
<td></td>
<td>aux-M</td>
<td>(9s)</td>
<td>0.050</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>aux-L</td>
<td>(12s)</td>
<td>0.022</td>
<td>2.32</td>
</tr>
</tbody>
</table>

The first value is for $s$ functions, the second is for $p$ functions.
DGELES with the parameter RCOND set to machine precision. In this subroutine, the effective rank of \( A \) is determined by treating as zero those singular values which are less than RCOND times the largest singular value. Whenever rank-deficiency was detected, we adjusted the auxiliary exponent \( \zeta_0 \) to restore the full rank. As a result, the basis sets of Table I are such that no matrix \( A \) is rank-deficient when using double precision. It is essential that even when the matrix \( A \) is rank-deficient, the ELP method still yields physically reasonable potentials. This is in contrast to the OEP method where rank deficiency may lead to unphysical potentials.

**B. Results**

To illustrate our method we computed exchange-only ELPs for several open-shell electron configurations of the He, Li, Be, and Na atoms. For Li and Na, we chose the ground state (the lowest \( ^2S \) term) and two Rydberg \( ^2S \) states produced by excitation of the unpaired electron to the lowest vacant \( s \) orbitals. We chose light atoms deliberately because single valence-electron excitations in few-electron systems have a more pronounced effect on exchange potentials than in heavy atoms.

For each state of these atoms, the Hartree–Fock wave function was computed using three different orbital basis sets (orb-S, orb-M, orb-L). For the subsequent ELP calculations, we paired each orbital basis set with one of the three auxiliary basis sets (aux-S, aux-M, aux-L).

The excited-state \( \alpha \)-spin ELPs are shown in Figs. 1–4. Each potential in these plots is shifted vertically to satisfy the relation

\[
\langle \psi_{\alpha \text{HOMO}}^\alpha | V_X^X | \psi_{\alpha \text{HOMO}}^\alpha \rangle = \langle \psi_{\alpha \text{HOMO}}^\alpha | \hat{V}_{X}^{\alpha} | \psi_{\alpha \text{HOMO}}^\alpha \rangle,
\]

where \( \psi_{\alpha \text{HOMO}}^\alpha \) is the Hartree–Fock HOMO and \( \hat{V}_{X}^{\alpha} \) is constructed with Hartree–Fock orbitals. This relation is the ELP adaptation of the exact constraint for exact exchange potentials discussed by Levy and Görling.

We see from Figs. 1–4 that \( \alpha \)-spin ELPs for the higher-lying states have small but distinct "bumps" at a distance of...
several bohrs from the nucleus. For the lowest states of each system, these bumps are either completely absent (He and Li) or are not expressed (Be and Na). The structure and relative ordering of the exchange potentials in Figs. 1–4 are reminiscent of those reported by Della Sala and Görling for various electronic states of the carbon atom, and by Cheng et al. for Rydberg states of the hydrogen atom. The plots also suggest that exchange-only ELPs for excited states are not drastically different from the potentials for the lowest state of the same symmetry, and that their similarly increases with system size. This is consistent with the common practice of using ground-state density-functional approximations for calculating excited-state properties.

We do not show here \( \beta \)-spin ELPs for Li, Be, and Ne because spin-down electrons in these atoms are not involved in the excitations. Furthermore, there is only one spin-down electron in \( ^2S \) states of Li and in \( ^3S \) states of Be, so that \( \beta \)-spin ELPs for these systems are just one-electron Coulomb potentials taken with a minus sign.

Tables II–V contain excited-state ELP energies computed with different basis sets and include reference values of the corresponding Hartree–Fock limits, whenever the latter are available. Our excited-state Hartree–Fock energies clearly converge to these limits as the size of the orbital basis set is increased. All the ELP energies reported here were calculated with full-rank matrices \( A \), so they should be reproducible exactly using robust double-precision linear solvers.

Tables II–V show that when the orbital basis set is fixed, the ELP energy generally decreases with increasing auxiliary basis set, but remains above the corresponding Hartree–Fock energy. Occasionally, it may happen that a larger auxiliary basis set corresponds to a slightly higher ELP energy

### Table II. Spin-restricted Hartree–Fock and ELP energies (in \( E_h \)) of the three lowest \( ^3S \) states of the He atom.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis sets</th>
<th>( 1s^2s )</th>
<th>( 1s^3s )</th>
<th>( 1s^4s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>orb-S</td>
<td>-7.427062</td>
<td>-7.303098</td>
<td>-7.26924</td>
</tr>
<tr>
<td>ELP</td>
<td>orb-S/aux-S</td>
<td>-7.426792</td>
<td>-7.302705</td>
<td>-7.26281</td>
</tr>
<tr>
<td></td>
<td>orb-S/aux-M</td>
<td>-7.426809</td>
<td>-7.302939</td>
<td>-7.262791</td>
</tr>
<tr>
<td></td>
<td>orb-S/aux-L</td>
<td>-7.426828</td>
<td>-7.302973</td>
<td>-7.262792</td>
</tr>
<tr>
<td>HF</td>
<td>orb-M</td>
<td>-7.432630</td>
<td>-7.310500</td>
<td>-7.274846</td>
</tr>
<tr>
<td>ELP</td>
<td>orb-M/aux-S</td>
<td>-7.432331</td>
<td>-7.308127</td>
<td>-7.274181</td>
</tr>
<tr>
<td></td>
<td>orb-M/aux-M</td>
<td>-7.432353</td>
<td>-7.309259</td>
<td>-7.274211</td>
</tr>
<tr>
<td></td>
<td>orb-M/aux-L</td>
<td>-7.432375</td>
<td>-7.309831</td>
<td>-7.274378</td>
</tr>
<tr>
<td>HF</td>
<td>orb-L</td>
<td>-7.432726</td>
<td>-7.310203</td>
<td>-7.274873</td>
</tr>
<tr>
<td>ELP</td>
<td>orb-L/aux-S</td>
<td>-7.432427</td>
<td>-7.308133</td>
<td>-7.273015</td>
</tr>
<tr>
<td></td>
<td>orb-L/aux-M</td>
<td>-7.432438</td>
<td>-7.309932</td>
<td>-7.273046</td>
</tr>
<tr>
<td></td>
<td>orb-L/aux-L</td>
<td>-7.432469</td>
<td>-7.309946</td>
<td>-7.273540</td>
</tr>
<tr>
<td>Numerical HF( ^a )</td>
<td>-7.432727</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exact nonrelativistic( ^b )</td>
<td>-7.478060</td>
<td>-7.354098</td>
<td>-7.318531</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \)Reference 64.  
\( ^b \)Reference 65.
than a smaller basis. This is because the ELP energy is not variational: The ELP minimizes the variance of the operator $(\nu_2^\sigma - \tilde{\nu}_2^\sigma)$, not the energy. Such a basis set effect occurs in the transition from the orb-M/aux-M to orb-M/aux-L ELP energy for the third excited state of the Be atom (Table IV). It should be also kept in mind that because of the last term in Eqs. (25) and (40), our Hartree–Fock and ELP energies depend not only on the orbital and auxiliary basis sets used for the desired excited state, but also on the quality of the orbital basis set(s) used for all the lower-lying states.

For the systems reported in Tables II–V, vertical excitation energies (relative to the ground state) predicted by the constrained variational Hartree–Fock (orb-L) and the excited-state ELP (orb-L/aux-L) methods are slightly lower than the corresponding time-dependent Hartree–Fock (TDHF/orb-L) values. The differences are 1.0–1.5 eV for He, 0.01–0.03 eV for Be, 0.2–0.3 eV for Li, and about 0.01 eV for Na. Neither the ELP nor TDHF excitation energies for these systems deviate by more than 1.1 eV from the exact values, He being the worst case.

IV. CONCLUSION

Our main message is that effective local potentials for excited states can be readily computed if excited-state Hartree–Fock wave functions are available. The latter may be easily obtained by the constrained variational excited-state Hartree Fock method of Sec. IIA. Given that the excited-state SCF and ground-state ELP methods have been already tested on molecules,28,36–38,42,43,56 we believe that the excited-state ELP method will be applicable to molecules as well, provided suitable basis sets are used. The physics of the problem demands that orbital and auxiliary basis sets used in ELP calculations for highly excited states contain diffuse basis functions. Such functions tend to complicate numerical solution of Eq. (33) since they make the matrix A effectively rank-deficient. We anticipate that these difficulties may be alleviated by using different orbital and different auxiliary basis sets for different states. This requires constructing overlap matrices for two distinct basis sets and, in principle, poses no difficulty. An ideal way to generate state-specific orbital basis sets would be to optimize individual exponents by minimizing the excited-state Hartree–Fock energy.35 For auxiliary basis sets, more experimentation is in order before one can advance specific recommendations.

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