Ensemble-Hartree-Fock Scheme for Excited States. The Optimized Effective Potential Method

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Abstract

We review the ensemble-Hartree-Fock (eHF) scheme for excited states. The single-particle eHF equations contain different potentials for the various orbitals, leading to off-diagonal Lagrange multipliers that cannot be transformed away as in the ground state case. Using the Optimized Effective Potential method we are able to construct a common local potential and the resulting theory is seen to describe accurately atomic excitation energies.

A comparison of the eHF theory with the ensemble-Kohn-Sham (eKS) scheme suggests a correction for the ensemble exchange and correlation energy functional, that helps improve greatly the numerical results of the eKS scheme.

1   Introduction

Ground state Hartree Fock (HF) theory not only has proven a valuable tool to calculate the ground state properties of electronic systems, but has also served as a starting point for more sophisticated approaches which deal with correlation, like configuration interaction methods and density functional

theory (DFT). Ground state HF theory is based on the Rayleigh-Ritz variational principle, which states that the expectation value of the Hamiltonian of the $N-$electron system (atomic units)

$$H = \sum_i \left[-\frac{\nabla_i^2}{2} + U_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_j{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \tag{1}$$

attains its minimum value for the true ground state energy E_0:

$$\langle \Psi | H | \Psi \rangle \geq E_0 \tag{2}$$

where, Ψ is any normalized $N-$electron antisymmetric state. Let us take $N^\uparrow$ and $N^\downarrow$ the number of spin up and spin down electrons in the ground state, $N = N^\uparrow + N^\downarrow$. In the (unrestricted) HF approximation, one substitutes a trial $N-$particle Slater determinant

$$\Phi_0 = \frac{1}{\sqrt{N!}} \det \left[\phi_1^\uparrow, \ldots, \phi_{N^\uparrow}^\uparrow; \phi_1^\downarrow, \ldots, \phi_{N^\downarrow}^\downarrow \right] \tag{3}$$

for Ψ and minimizes the expectation value $\langle \Phi_0 | H | \Phi_0 \rangle$ with respect to the spin-orbitals ϕ_j^σ of Φ_0. The minimization results in single particle Schrödinger-like equations which determine ϕ_j^σ:

$$h_{\Phi_0} \phi_j^\sigma(\mathbf{r}) = \varepsilon_j^\sigma \; \phi_j^\sigma(\mathbf{r}) \tag{4}$$

where,

$$\begin{aligned}
h_{\Phi_0} \phi_j^\sigma(\mathbf{r}) &= \left[-\frac{\nabla^2}{2} + U_{\text{ext}}(\mathbf{r}) + \sum_{s=\uparrow,\downarrow} \sum_{\phi_n^s \in \Phi_0} \int d^3 r' \frac{|\phi_n^s(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \phi_j^\sigma(\mathbf{r}) \\
&\quad - \sum_{\phi_n^\sigma \in \Phi_0} \int d^3 r' \frac{\rho_n^\sigma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_j^\sigma(\mathbf{r}')
\end{aligned} \tag{5}$$

and

$$\rho_n^\sigma(\mathbf{r}, \mathbf{r}') \equiv \phi_n^\sigma(\mathbf{r}) \; \phi_n^{\sigma*}(\mathbf{r}') \tag{6}$$

In HF theory, one assigns the physical meaning of an independent electron to each occupied spin-orbital ϕ_j^σ.

The extension of the HF scheme to excited states is more subtle. For example, if one wants to obtain information about the first excited state, the Rayleigh-Ritz variational principle dictates that the trial Slater determinant to approximate the first excited state must be orthogonal to the

2

exact (unknown) ground state. If, instead, one imposes the orthogonality constraint on the Slater determinant Φ_0 which approximately represents the ground state, then the initial error will multiply. Nevertheless, the physical meaning of excited electrons, is often assigned to the eigen-orbitals of h_{Φ_0} which are not occupied in Φ_0. To ascertain that his is clearly problematic, consider that each unoccupied orbital lies in the field of N rather than $N-1$ electrons, causing the virtual orbitals of h_{Φ_0} to be too diffuse. Various methods to overcome the problem have appeared [1, 2, 3], within ground state HF theory.

An elegant method to study low excitations in HF theory is to abandon the Rayleigh-Ritz variational principle and use the ensemble variational principle (or subspace, or trace variational principle), first used in the foundation of DFT for excited states by Theophilou [4] and later by Gross, Oliveira and Kohn [5, 6]. Considering for simplicity only the ground state and the first excited state Ψ_0, Ψ_1 of H, the minimum principle states that the trace $E_\omega[\Psi, \Psi']$

$$E_\omega[\Psi, \Psi'] = (1 - \omega) \langle \Psi | H | \Psi \rangle + \omega \langle \Psi' | H | \Psi' \rangle \tag{7}$$

with Ψ, Ψ' orthonormal and $0 < \omega \le 1/2$, attains its minimum value when $\Psi = \Psi_0$ and $\Psi' = \Psi_1$. This statement holds true for any value of ω in the interval $0 < \omega \le 1/2$. Theophilou's subspace or equi-ensemble theory was restricted to the value $\omega = 1/2$, where the weight of the excited state is maximized.

2 Ensemble Hartree-Fock equations

Consider for simplicity only the ground state and the lowest single particle excitation of an $N-$electron system described by H. We may take the highest occupied orbital spin up and non degenerate. The Slater determinant representing the lowest excitation will be

$$\Phi_1 = \frac{1}{\sqrt{N!}} \det \left[\phi_1^\uparrow, \ldots, \phi_{N\uparrow-1}^\uparrow, \phi_{N\uparrow+1}^\uparrow; \phi_1^\downarrow, \ldots, \phi_{N\downarrow}^\downarrow \right] \tag{8}$$

Next, form the trace, with $0 < \omega \le 1/2$:

$$E_\omega = (1 - \omega)\langle \Phi_0 | H | \Phi_0 \rangle + \omega \langle \Phi_1 | H | \Phi_1 \rangle \tag{9}$$

The trace E_ω can be written in terms of the spin orbitals:

$$
\begin{aligned}
E_\omega \;=\; & -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{\phi_n^\sigma\in\Phi_0}\int d^3r\;\phi_n^{\sigma*}(\mathbf{r})\;\nabla^2\phi_n^\sigma(\mathbf{r}) + \int d^3r\;U_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) && (10)\\
& -\frac{\omega}{2}\int d^3r\;\phi_{N^\uparrow+1}^{\uparrow*}(\mathbf{r})\;\nabla^2\phi_{N^\uparrow+1}^\uparrow(\mathbf{r}) + \frac{\omega}{2}\int d^3r\;\phi_{N^\uparrow}^{\uparrow*}(\mathbf{r})\;\nabla^2\phi_{N^\uparrow}^\uparrow(\mathbf{r})\\
& +\frac{1}{2}\int\int d^3r\,d^3r'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\omega(1-\omega)}{2}\int\int d^3r\,d^3r'\frac{g^\uparrow(\mathbf{r})g^\uparrow(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\
& -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\int\int d^3r\,d^3r'\frac{|\rho^\sigma(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} - \frac{\omega(1-\omega)}{2}\int\int d^3r\,d^3r'\frac{\left|g^\uparrow(\mathbf{r},\mathbf{r}')\right|^2}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}
$$

where, $g^\uparrow(\mathbf{r},\mathbf{r}') = \rho_{N^\uparrow+1}^\uparrow(\mathbf{r},\mathbf{r}') - \rho_{N^\uparrow}^\uparrow(\mathbf{r},\mathbf{r}')$, $g^\uparrow(\mathbf{r}) = g^\uparrow(\mathbf{r},\mathbf{r})$, $\rho^\downarrow(\mathbf{r},\mathbf{r}') = \sum_{\phi_n^\downarrow\in\Phi_0}\rho_n^\downarrow(\mathbf{r},\mathbf{r}')$, $\rho^\uparrow(\mathbf{r},\mathbf{r}') = \sum_{\phi_n^\uparrow\in\Phi_0}\rho_n^\uparrow(\mathbf{r},\mathbf{r}') + \omega\,g^\uparrow(\mathbf{r},\mathbf{r}')$, $\rho(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow}\rho^\sigma(\mathbf{r},\mathbf{r})$.

Based on the ensemble minimum principle, the ensemble-Hartree-Fock (eHF) equations for the ground and the lowest excited states are obtained by minimizing the trace with respect to the spin-orbitals [7, 8]. Observe that not all spin-orbitals appear symmetrically in E_ω. This implies that the single particle equations for the various orbitals of the same spin are inhomogeneous i.e., the equations have different potentials, and consequently nondiagonal Lagrange multipliers appear that cannot be chosen to vanish with a suitable unitary transformation of the minimizing orbitals [8].

2.1 The Optimized Effective Potential Method

Obviously, it would be desirable to overcome the difficulties associated with a scheme which involves different Hamiltonians for the various orbitals. To this end, we chose to minimize the trace E_ω, requiring that the orbitals of the same spin form the lowest $N^\uparrow + 1$ and $N^\downarrow$ single-particle eigenstates of some common (for each spin) local potential $V^\uparrow$ and $V^\downarrow$ to be determined. This constitutes the Optimized Effective Potential (OEP) method [9, 10] for the eHF scheme which introduces an additional approximation to eHF.

In the following, we shall derive the equations determining $V^\uparrow$, $V^\downarrow$.

In the OEP picture, E_ω is a functional of the local potentials, $E_\omega = E_\omega[V^\uparrow, V^\downarrow]$. The functional derivative $\delta E_\omega/\delta V^\sigma(\mathbf{r})$ is defined by the limit

$$
\lim_{\lambda\to 0}\frac{E_\omega[V^\sigma+\lambda\delta V^\sigma, V^{\sigma'}] - E_\omega[V^\sigma, V^{\sigma'}]}{\lambda} = \int d^3r\;\frac{\delta E_\omega}{\delta V^\sigma(\mathbf{r})}\delta V^\sigma(\mathbf{r}), \quad (11)
$$

where, $\sigma = \uparrow, \downarrow, \sigma' = \downarrow, \uparrow$.

In order to be well defined, the functional derivative in (11) must be independent of the choice of δV^σ. Denote here too by $\{\phi_n^\sigma\}$ the single-particle eigenstates of V^σ.

$$\left[-\frac{\nabla^2}{2} + V^\sigma(\mathbf{r}) \right] \phi_n^\sigma(\mathbf{r}) = \epsilon_n^\sigma \, \phi_n^\sigma(\mathbf{r}) \tag{12}$$

Then, for $0 < \lambda \ll 1$, the eigenstates of $V^\sigma + \lambda \delta V^\sigma$ will be given by

$$\phi_{n,\lambda}^\sigma(\mathbf{r}) = \phi_n^\sigma(\mathbf{r}) - \lambda \int d^3 r' \, \delta V^\sigma(\mathbf{r}') \, G_n^\sigma(\mathbf{r}, \mathbf{r}') \, \phi_n^\sigma(\mathbf{r}')$$

where

$$G_n^\sigma(\mathbf{r}, \mathbf{r}') = \sum_{m=1 \, m \neq n}^{\infty} \frac{\rho_m^\sigma(\mathbf{r}, \mathbf{r}')}{\epsilon_m^\sigma - \epsilon_n^\sigma}$$

Substituting the above in (11) and using Eq. (12) we can calculate the functional derivatives:

$$
\begin{aligned}
\frac{\delta E_\omega}{\delta V^\sigma(\mathbf{r})} &= \int d^3 r' F^\sigma(\mathbf{r}; \mathbf{r}', \mathbf{r}') \left[V^\sigma(\mathbf{r}') - U_{\text{ext}}(\mathbf{r}') - \int \frac{d^3 r'' \rho(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \right] \\
&\quad + \int \int d^3 r' d^3 r'' \frac{F^\sigma(\mathbf{r}; \mathbf{r}', \mathbf{r}'') \rho^\sigma(\mathbf{r}'', \mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|} \\
&\quad - \delta_{\sigma,\uparrow} \, \omega(1 - \omega) \int d^3 r' B^\uparrow(\mathbf{r}; \mathbf{r}', \mathbf{r}') \int \frac{d^3 r'' g^\uparrow(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \\
&\quad + \delta_{\sigma,\uparrow} \, \omega(1 - \omega) \int \int d^3 r' d^3 r'' \frac{B^\uparrow(\mathbf{r}; \mathbf{r}', \mathbf{r}'') g^\uparrow(\mathbf{r}'', \mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|}
\end{aligned}
$$

where, $\delta_{\sigma,\uparrow} = 1$ if $\sigma = \uparrow$, $\delta_{\sigma,\uparrow} = 0$ if $\sigma = \downarrow$ and

$$
\begin{aligned}
B^\uparrow(\mathbf{r}; \mathbf{r}', \mathbf{r}'') &= G_{N\uparrow+1}^\uparrow(\mathbf{r}', \mathbf{r}) \rho_{N\uparrow+1}^\uparrow(\mathbf{r}, \mathbf{r}'') + G_{N\uparrow+1}^\uparrow(\mathbf{r}, \mathbf{r}'') \rho_{N\uparrow+1}^\uparrow(\mathbf{r}', \mathbf{r}) \\
&\quad - G_{N\uparrow}^\uparrow(\mathbf{r}', \mathbf{r}) \rho_{N\uparrow}^\uparrow(\mathbf{r}, \mathbf{r}'') - G_{N\uparrow}^\uparrow(\mathbf{r}, \mathbf{r}'') \rho_{N\uparrow}^\uparrow(\mathbf{r}', \mathbf{r}) \\
F^\downarrow(\mathbf{r}; \mathbf{r}', \mathbf{r}'') &= \sum_{n=1}^{N^\downarrow} \left[G_n^\downarrow(\mathbf{r}', \mathbf{r}) \rho_n^\downarrow(\mathbf{r}, \mathbf{r}'') + G_n^\downarrow(\mathbf{r}, \mathbf{r}'') \rho_n^\downarrow(\mathbf{r}', \mathbf{r}) \right] \\
F^\uparrow(\mathbf{r}; \mathbf{r}', \mathbf{r}'') &= \sum_{n=1}^{N^\uparrow} \left[G_n^\uparrow(\mathbf{r}', \mathbf{r}) \rho_n^\uparrow(\mathbf{r}, \mathbf{r}'') + G_n^\uparrow(\mathbf{r}, \mathbf{r}'') \rho_n^\uparrow(\mathbf{r}', \mathbf{r}) \right] + \omega \, B^\uparrow(\mathbf{r}; \mathbf{r}', \mathbf{r}'')
\end{aligned}
$$

$B^{\uparrow}(\mathbf{r}; \mathbf{r}', \mathbf{r}'')$ and $F^{\sigma}(\mathbf{r}; \mathbf{r}', \mathbf{r}'')$ are Hermitian with respect to the second pair of arguments: $[B^{\uparrow}(\mathbf{r}; \mathbf{r}', \mathbf{r}'')]^* = B^{\uparrow}(\mathbf{r}; \mathbf{r}'', \mathbf{r}')$ and $[F^{\sigma}(\mathbf{r}; \mathbf{r}', \mathbf{r}'')]^* = F^{\sigma}(\mathbf{r}; \mathbf{r}'', \mathbf{r}')$. Consequently $B^{\uparrow}(\mathbf{r}; \mathbf{r}', \mathbf{r}')$ and $F^{\sigma}(\mathbf{r}; \mathbf{r}', \mathbf{r}')$ are real.

The minimizing potentials of E_ω are determined by the OEP integral equations

$$\frac{\delta E_\omega}{\delta V^\sigma(\mathbf{r})} = 0 \ , \ \sigma = \uparrow, \downarrow \tag{13}$$

Applying the popular mean field approximation by Krieger Li and Iafrate [11, 12] to simplify (13), we have calculated the total ensemble energies of various atoms and present the results in Table 1. An equi-ensemble ($\omega = 1/2$) has been chosen. The states in each ensemble are proper eigenfunctions of the total spin [13] and consequently we had to use a different potential for each ensemble. These potentials were derived in a similar way to Eqs. (13) and details of the derivation will be published elsewhere.

The experimental data in the last column are taken from the NIST database for Atomic Spectroscopy [14]. The eHF results give upper bounds to the experimental values as expected.

The ensemble-Kohn-Sham (eKS) scheme proposed by Theophilou [4] and later by Gross, Oliveira and Kohn [5, 6] was also based on the ensemble variational principle. The basic quantity in the formulation of the theory is the ensemble (average) density $\rho(\mathbf{r})$ and in the eKS scheme, the interacting system with ensemble density $\rho(\mathbf{r})$ and energy E_ω is mapped to a non-interacting one with the same ensemble density, and energy.

A comparison of the eHF and the eKS theories reveals that the definition of the ensemble Hartree energy

$$\frac{1}{2} \int \int d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{14}$$

contains an unphysical interaction between the orbitals $\phi_{N\uparrow}^{\uparrow}$ and $\phi_{N\uparrow+1}^{\uparrow}$, which, in the non-interacting picture, are never occupied in the same configuration. We called this unphysical interaction the ghost-interaction and clearly the ensemble exchange and correlation energy functional must correct for it [15]. The reader is also referred to the recent reformulation of the the OEP method for ensembles of excited states by Nagy [16].

Neglecting correlation but including exchange, the ground state (gs) KS scheme reduces to the gs exchange-only (x-only) KS scheme. When exchange is included exactly, through the Fock expression, the solution of the (gs) x-only KS scheme coincides with solution of OEP integral equations to

Atom	Ensemble	Noof states	eHF	eKS	Exper.
He	$\{1s^2\}^1S$; $\{1s2s\}^1S$	2	-67.456	-68.463	-68.708
He	$\{1s2s\}^3S$; $\{1s3s\}^3S$	2	-57.606	-57.606	-57.769
He	$\{1s2s\}^3S$; $\{1s2p\}^3P$	2	-58.613	-58.613	-58.640
He	$\{1s2s\}^3S$; $\{1s2p\}^3P$	4	-58.313	-58.313	-58.340
Li	$\{1s^22s\}^2S$; $\{1s^22p\}^2P$	4	-200.953	-202.287	-202.096
Li	$\{1s^22s\}^2S$; $\{1s^23s\}^2S$	2	-200.382	-201.661	-201.797
C^{2+}	$\{1s^22s^2\}^1S$; $\{1s^22s2p\}^3P$	4	-986.616	-989.31	-989.256

Table 1: Equiensemble total energies for various atoms in eV units. The ensemble configuration and dimensionality are shown in the second and third columns. In the last column the total energy of the ensemble is shown. In the case of an n-dimensional subspace with E_i, $1 \leq i \leq n$, the n lowest eigenvalues, the total energy is equal to $\frac{1}{n} \sum_{i=1}^{n} E_i$.

minimize the (gs) HF energy expression. We can say rather loosely that the (gs) exact x-only KS scheme coincides with the (gs) HF-OEP method. In the case of excited states, the eHF-OEP method we just presented, is found to coincide with the exact x-only eKS scheme, only when the spurious ghost interaction is corrected properly [15]. This is actually how we were led to discover the presence of the ghost interaction in the eKS formulation. Comparing the two theories, the eHF-OEP method and the eKS scheme, the latter in principle, may account for correlation effects, provided an appropriate *ensemble* correlation functional is available. In the absence however of any approximation, we chose to employ for our calculation the approximate gs correlation functional of Colle and Salvetti [17].

In the fifth column in Table 1, we give the results of the eKS calculation, with the ghost interaction corrected and using the approximate gs Colle-Salvetti correlation functional.

References

[1] H.J. Silverstone and M.L. Yin, J. Chem. Phys. **49**, 2026 (1968)

[2] W.J. Hunt and W.A. Goddard III, Chem. Phys. Lett. **6**, 414 (1969)

[3] S. Huzinaga and C. Arnau Phys. Rev. A **1**, 1285 (1970)

[4] A.K. Theophilou, J. Phys. C, **12**, 5419 (1979)

[5] E.K.U. Gross, L.N. Oliveira and W. Kohn, Phys. Rev. A **37**, 2805 (1988); *ibid* 2809 (1988)

[6] L.N. Oliveira, E.K.U. Gross and W. Kohn, Phys. Rev. A **37**, 2821 (1988)

[7] A.K. Theophilou, 'Recent Developments in Condensed Matter Physics', Vol.2, edited by J.T. DeVreese, L.F. Lemmens, V.E. Doren and J. Van Royen, Plenum, New York, p.125 (1981)

[8] N. Gidopoulos and A.Theophilou, Phil. Mag. B **69**, 1067 (1994)

[9] R.T. Sharp and G.K. Horton, Phys. Rev. **90**, 317 (1953)

[10] J.D. Talman and W.F. Shadwick, Phys. Rev. A **14**, 36 (1976)

[11] J.B. Krieger, Y. Li and G.J. Iafrate, Phys. Rev. A **45**, 101 (1991); *ibid* **46**, 5453 (1992); *ibid* **47**, 165 (1993)

[12] J.B. Krieger, Y. Li and G.J. Iafrate, in 'Density Functional Theory' edited by R.M. Dreizler and E.K.U. Gross, Plenum Press, New York, p.191, (1995)

[13] A.K. Theophilou and P.G. Papaconstantinou, Phys. Rev. A **61**, 22502 (2000)

[14] National Institute of Standards and Technology, U.S. Department of Commerce (1995)

[15] N.I. Gidopoulos, P.G. Papaconstantinou and E.K.U. Gross, Phys. Rev. Lett., scheduled to appear in the 7th of January issue (2002).

[16] Á. Nagy, J. Phys. B: At. Mol. Opt. Phys. **34**, 2363, (2001).

[17] R. Colle and D. Salvetti, Theoret. Chim. Acta **37**, 329 (1975); *ibid* **53**, 55 (1979)