Symmetry preserving and improved energy states derived from asymmetric Hartree-Fock

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Abstract. Symmetry preserving Hartree-Fock (HF) states, give higher energies than those of the unrestricted HF. However, in analyzing an unrestricted HF state (UHF) in terms of states transforming according to the Irreducible Representations of the exact Hamiltonian of a many electron system, we prove that some of these states have lower energy than the initial UHF state. The case of rotational and spin symmetries are discussed.

1. Introduction

One of the main achievement of Quantum Mechanics is the calculation of the properties of atoms, molecules and solids. Most of these calculations deal with the ground state, which is not only an eigenstate of the Hamiltonian \( H \), but it is also the minimizing state of the energy functional \( E(\Psi) = \langle \Psi | H | \Psi \rangle \). As it is practically impossible to obtain the exact eigenstates, even in the case of the Helium atom, which has only two electrons, many approximations appeared. One of them is the Hartree-Fock approximation, which is based on single Slater determinant minimization. A simplification of this is the Optimized Effective Potential Approximation [1, 2, 3, 4], where the space of the minimizing states is restricted to those obtained by an effective potential. Another popular method is the Kohn and Sham method [5] based on a theorem showing that there is one to one correspondence between the ground state and its density [6].

The main disadvantage of this theory is that no functionals of the exchange and correlation energy exist, which are sufficiently accurate. Many simplifications of the many electron theory have their origin in the symmetry of the Hamiltonian, resulting from the fact that it deals with identical particles. Thus, the many electron Hamiltonian is invariant under any permutation of the space and spin variables and therefore the eigenstates of the Hamiltonian belong to the irreducible representations (Ireps) of the permutation group. Fortunately only the antisymmetric Irrep appears in nature. Another symmetry which is always present, when no inhomogeneous magnetic field is applied, is spin symmetry. Thus, the energy eigenstates of atoms, molecules and solids are also eigenstates of \( S^2 \) and \( S_z \). Other symmetries may appear, like e.g. the spherical symmetry in atoms and space group symmetries in solids. Some, molecules have point group symmetries, whereas two-atom molecules have axial symmetry. These symmetries are geometric in nature and arise because of the symmetries originating from the positions of the nuclei.

A lot of theoretical work in the early development of the many-electron theory has been developed by Löwdin [7, 8, 9, 10, 11]. Löwdin, extended HF, by projecting out of a single Slater determinant (Sladet) an eigenstates \( |\Psi^S_M\rangle \) of \( S^2 \). This state is not a single Sladet but a linear
combination of such states. The resulting energy functional $\langle \Psi^S_k | H | \Psi^S_M \rangle$ was next minimized with respect to the orbitals, giving energies lower than those of UHF [12, 13].

In Section 2, we shall show how from the asymmetric solutions of UHF, one can obtain solutions which belong to a definite Irrep of the symmetry group of the Hamiltonian and also have lower energies. The advantage with respect to the extended HF, is that one uses the standard UHF solutions, to improve on energy and quality. We deal with the example of spherical symmetry, whereas the problem of spin symmetry with numerical examples is treated in a sequel paper [14].

2. The Method

We consider the many electron Hamiltonian $H$,

$$H = T + V + H_{\text{int}}$$

where $T$ is the kinetic energy operator, $V$ is the external potential and $H_{\text{int}}$ is the electron-electron interaction operator, $H_{\text{int}} = H^t_{\text{int}} + H^s_{\text{int}}$

$$H^s_{\text{int}} = \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_{s\uparrow}(\mathbf{r}) \psi_{s\uparrow}(\mathbf{r}') \psi_{s\downarrow}(\mathbf{r}') \psi_{s\downarrow}(\mathbf{r})$$

where $\psi_{s\uparrow}(\mathbf{r})$, $\psi_{s\downarrow}(\mathbf{r})$ are the fermion field creation and annihilation operators with $s$ the spin index, which takes the values $\uparrow$ and $\downarrow$. Let us define the functional

$$E(\Phi) = \langle \Phi | H | \Phi \rangle, \quad |\Phi > > \epsilon S_{sl},$$

with $S_{sl}$ the space of $N - \text{particle}$ Slater states $|\Phi_M > = |\varphi^1_1, \varphi^1_2, ..., \varphi^1_M; \varphi^1_1, \varphi^2_2, ... \varphi^1_1 \rangle >$ corresponding to the Sladet determinants (Sladets)

$$\Phi_M(\mathbf{r}_1, ..., \mathbf{r}_N; \varphi^1_1, \varphi^1_2, ..., \varphi^1_M; \varphi^1_1, \varphi^2_2, ... \varphi^1_1) = \frac{1}{\sqrt{N!}} \det \{ \varphi^1_{l_j} \}_{j=1}^N,$$

where the $\varphi^i_l(\mathbf{r})$ are one-particle wave functions named as spin orbitals and $M = (k - l)/2$ is the eigenstate of $L_z$.

The above functional can be expressed as

$$E(\Phi) = \langle \Phi | T | \Phi \rangle + \langle \Phi | V | \Phi \rangle + E_h(\Phi) + E_x(\Phi)$$

where $E_h(\Phi) = E^{\uparrow\uparrow}_h(\Phi) + E^{\downarrow\downarrow}_h(\Phi) + 2E^{\uparrow\downarrow}_h(\Phi)$ and the suffix $M$ has been omitted for the sake of simplicity of notation,

$$E^{\alpha\beta}_h(\Phi) = \frac{1}{2} \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho^\alpha_{\Phi}(\mathbf{r}) \rho^\beta_{\Phi}(\mathbf{r}')$$

is the electrostatic (Hartree) energy due to the electron density $\rho_{\Phi}(\mathbf{r}) = \rho^\uparrow_{\Phi}(\mathbf{r}) + \rho^\downarrow_{\Phi}(\mathbf{r})$ and the indices $\alpha$ and $\beta$ take the values $\uparrow$ and $\downarrow$.

It is to be noted that the exchange energy $E_x(\Phi) = E^{\uparrow\downarrow}_x(\Phi) + E^{\downarrow\uparrow}_x(\Phi)$, with

$$E^{\alpha\beta}_x(\Phi) = \frac{1}{2} \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho^\alpha_{\Phi}(\mathbf{r}) \rho^\beta_{\Phi}(\mathbf{r}', \mathbf{r})$$

does not include a cross term. Thus the up and down terms of $E(\Phi)$, are coupled only through the Hartree term $E^{\uparrow\downarrow}_h$. In the above expressions $\rho^\alpha_{\Phi}(\mathbf{r}, \mathbf{r}') = \langle \Phi | \psi^\alpha(\mathbf{r}) \psi^\alpha(\mathbf{r}') | \Phi \rangle$ is the density
matrix of the state $|\Phi\rangle$ and $\rho^\alpha_\Phi (\mathbf{r}) = \rho^\alpha_\Phi (\mathbf{r}, \mathbf{r})$ is the electron density of spin $\alpha$. The explicit form of $\rho^\alpha_\Phi (\mathbf{r}, \mathbf{r})$ is

$$\rho^\alpha_\Phi (\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{k_a} \varphi^\alpha_i (\mathbf{r})^* \varphi^\alpha_i (\mathbf{r}') , \quad k_1 = k, \ k_1 = l$$

(8)

With the above expression of $E(\Phi)$, one does not have to add the constraint that $|\Phi\rangle$ is a Slater state. After applying the variational principle, we find that the minimizing state of $E(\Phi)$ is not an eigenstate of $H$, but of the Hartree-Fock Hamiltonian $H^hf$, where $T$ is the kinetic energy operator, $V$ is the external potential and $V_h (\Phi)$ is the Hartree potential operator

$$V_h (\Phi) = \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} (\rho_\Phi (\mathbf{r}') \psi^\dagger (\mathbf{r}) \psi (\mathbf{r}) + \psi^\dagger (\mathbf{r}) \psi (\mathbf{r}'))$$

(10)

and $V_x (\Phi)$ is the exchange operator

$$V_x (\Phi) = \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|}(\rho_\Phi (\mathbf{r}, \mathbf{r}') \psi^\dagger (\mathbf{r}) \psi (\mathbf{r}) + \rho_\Phi (\mathbf{r}, \mathbf{r}') \psi^\dagger (\mathbf{r}) \psi (\mathbf{r}'))$$

(11)

Note that the HF operator $H^hf$ is not linear since $V_h (\Phi)$ and $V_x (\Phi)$ depend on $|\Phi\rangle$. Thus the HF solutions are qualitatively different with respect to symmetry from the eigenstates of the exact Hamiltonian. To see this let $H$ be invariant under a symmetry group $G$, i.e., $gHg^{-1} = H$, for all $g \in G$ [15]. Then, if a state $|\Psi^\Gamma_\gamma\rangle$ transform according to the $\Gamma$ Irrep of $G$, then one can easily verify by direct calculation that the state $H|\Psi^\Gamma_\gamma\rangle$ transforms according to the same Irrep since $gH|\Psi^\Gamma_\gamma\rangle = gHg^{-1}g|\Psi^\Gamma_\gamma\rangle = Hg|\Psi^\Gamma_\gamma\rangle$. This is not the case with the HF operator $H^hf$ since $\rho^\alpha_\Phi (\mathbf{r}, \mathbf{r}')$ does not transform according to the identity Irrep of $G$, except in the special case that $|\Phi\rangle$ itself belongs to the identity Irrep. To verify this statement take the example of spherical symmetry and $l = 1$, for the case that the unfilled shell has only two particles with $m = 0$ and $m = 1$. Then $\varphi^m_1 (\mathbf{r}) = \varphi^1 (\mathbf{r})Y^m_1 (\theta, \phi)$ and after introducing the explicit form of the spherical harmonic $Y^m_1 (\theta, \phi)$ we have

$$\rho^\alpha_\Phi (\mathbf{r}, \mathbf{r}') = \sum_{m=0}^1 \varphi^m_1 (\mathbf{r})^* \varphi^m_1 (\mathbf{r}') = \varphi^1 (\mathbf{r}) \varphi^1 (\mathbf{r}') \frac{1}{2\pi} \cos \theta \cos \theta' + \sin \theta \sin \theta' \epsilon (\phi - \phi')$$

(12)

This operator does not transform according to the identity Irrep since, even for the case that $\mathbf{r} = \mathbf{r}'$, we get a density which depends on the angle $\theta$ and hence it has no spherical symmetry.

To see our argument about symmetry more explicitly, we consider the one-particle HF equation for a spherically symmetric external potential $V (\mathbf{r}) = V (r)$.

$$-\frac{1}{2} \nabla^2 \varphi^\alpha_i (\mathbf{r}) + V (\mathbf{r}) \varphi^\alpha_i (\mathbf{r}) + V_h (\mathbf{r}; \Phi) \varphi^\alpha_i (\mathbf{r}) + \int d^3r' \rho^\alpha_\Phi (\mathbf{r}, \mathbf{r}') \varphi^\alpha_i (\mathbf{r}') = \varepsilon_i \varphi^\alpha_i (\mathbf{r})$$

(13)

which determines the $\varphi^\alpha_i (\mathbf{r})$ of the minimizing Sladet. Then it is obvious that the $\varphi^\alpha_i (\mathbf{r})$ are not eigenstates of $L^2$ because the Hartree and exchange operators are not spherically symmetric, except in the case of filled shells, where

$$\rho^\alpha_\Phi (\mathbf{r}, \mathbf{r}') = \sum_{m=-l}^l \varphi^l_m (\mathbf{r})^* \varphi^l_m (\mathbf{r}') = \varphi^l (\mathbf{r}) \varphi^l (\mathbf{r}') \frac{2l+1}{4\pi} P^l (\frac{\mathbf{r} \cdot \mathbf{r}'}{|\mathbf{r} \cdot \mathbf{r}'|})$$

(14)
One can easily verify that $\rho_0^q(r,r')$ is invariant under simultaneous rotations of $r$ and $r'$.

From the above we conclude that the unrestricted HF ground state does not transform according to a definite Irrep of the symmetry group of the exact Hamiltonian, unless one imposes the constraint that the minimization is restricted in a subspace $S^\Gamma_\gamma$ the wavefunctions of which transform according to Irrep $\Gamma$ of $G$. Let us define this space as $S^\Gamma_\gamma$. This is a subspace of the space of single $N$–particle determinants $S_{sl}$. Therefore, the energy minimum of $E(\Phi^\Gamma_\gamma) = \langle \Phi^\Gamma_\gamma | H | \Phi^\Gamma_\gamma \rangle$ is larger or equal to min $E(\Phi)$ with $|\Phi\rangle$ in $S_{sl}$ which contains $S^\Gamma_\gamma$.

The HF under the subspace constraint is called restricted HF (RHF) while the one without the constraint is called unrestricted HF (UHF). In the following we shall call a state asymmetric if it does not transform according to a definite Irrep of the symmetry group $G$ of the Hamiltonian.

We shall show that one can use the asymmetric solutions of UHF to get lower energies than $E(\Phi_{UHF})$. Further, the new solutions belong to definite irreps of the symmetry group of $H$, having thus the transformation properties of the exact solutions. To prove this let us denote by $|\Phi\rangle$ the asymmetric $|\Phi_{UHF}\rangle$ state. Then, we can express $|\Phi\rangle$ in terms of its Irrep components $|\Psi^\Gamma_\gamma\rangle$, which in general are not single Sladets, but linear combinations of them,

$$|\Phi\rangle = \sum_{\Gamma, \gamma} c^{\Gamma}_{\gamma}|\Psi^\Gamma_\gamma\rangle.$$  \hspace{1cm} (15)

In the above expansion the $|\Psi^\Gamma_\gamma\rangle$ are the maximum overlap states of the functional $F(\Psi^\Gamma_\gamma) = |\langle \Phi | \Psi^\Gamma_\gamma \rangle|^2$. Thus, only one state enters from each subspace $S^\Gamma_\gamma$. To prove this we must show that any other state $|X^\Gamma_\gamma\rangle$ which is orthogonal to $|\Psi^\Gamma_\gamma\rangle$ is also orthogonal to $|\Phi\rangle$. Since $|\Psi^\Gamma_\gamma\rangle$ is the maximizing state of the functional $F(\Psi^\Gamma_\gamma)$ it follows that

$$\lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \{ \langle \Phi | \Psi^\Gamma_\gamma + \epsilon X^\Gamma_\gamma \rangle - \langle \Phi | \Psi^\Gamma_\gamma \rangle \} = 0$$ \hspace{1cm} (16)

and after taking the limits we find $\langle X^\Gamma_\gamma | \Phi \rangle = 0$, q.e.d.

By taking into account that $H|\Psi^\Gamma_\gamma\rangle$ is a state transforming according to the same Irrep as $|\Psi^\Gamma_\gamma\rangle$, since $gHg^{-1} = H$, from the orthogonality relation of states belonging to different irreps, it follows that

$$\langle \Psi^A_\alpha | H | \Psi^\Gamma_\gamma \rangle = E^A_\alpha \delta_{\alpha \gamma}$$

and

$$E(\Phi) = \sum_{\Gamma, \gamma} |c^{\Gamma}_{\gamma}|^2 < \Psi^\Gamma_\gamma | H | \Psi^\Gamma_\gamma \rangle = \sum_{\Gamma, \gamma} |c^{\Gamma}_{\gamma}|^2 E^\Gamma + \sum_{\Gamma} |c^\Gamma|^2 E^\Gamma,$$  \hspace{1cm} (17)

where $|c^\Gamma|^2 = \sum_{\gamma} |c^{\Gamma}_{\gamma}|^2$.

We shall show that there is at least one $E^\Gamma$ which is smaller than $E(\Phi)$, unless all $E^\Gamma = E(\Phi)$ for all $\Gamma$. This statement is obvious since if we consider the opposite we arrive at a contradiction. Thus, let $E^\Gamma \geq E(\Phi)$ and for some $B$, $E^B > E(\Phi)$. Then by taking into account that $\sum_{\Gamma} |c^\Gamma|^2 = 1$, we have

$$E(\Phi) = \sum_{\Gamma} |c^\Gamma|^2 E^\Gamma > \sum_{\Gamma} |c^\Gamma|^2 E(\Phi) = E(\Phi).$$  \hspace{1cm} (18)

This inequality implies $E(\Phi) > E(\Phi)$, which is a contradiction. Hence there is at least one $|\Psi^A_\alpha\rangle$ having energy less than that of the unrestricted HF.

In general it is not possible to judge which Irrep gives the lowest energy. Practice has shown that in most cases, the ground state is not degenerate and therefore one has to look for the one-dimensional irreps. This is the case for molecules at their equilibrium positions because of the Jahn-Teller effect, but for atoms in some cases we have degenerate ground states.
From the above we conclude that it is possible to extract some of the correlation energy, $E_c$, from the usual UHF approximation. Obviously, one has to find the way to determine the $|\Psi^\Gamma_\gamma >$ from the $|\Phi >$. This can be done by the projection theorem [15]:

$$|\Psi^\Gamma_\gamma > = \frac{N_\Gamma}{N_G} \sum g D^\Gamma_{\gamma g}(g)|\Psi >,$$

(19)

where $D^\Gamma_{\gamma g}(g)$ is the $\gamma a$ matrix element of the $N_\Gamma \dim$ Irrep $\Gamma$ of the group $G$ the order of which is $N_\Gamma$. In most cases there are easier ways to determine the $|\Psi^\Gamma_\gamma >$. Examples for the case of spin symmetry are given in Ref [16] and details about the procedure to extract $E_c$ from UHF are given in a sequel paper [14]. In the present paper we shall consider the case of spherical symmetry, applicable for atoms. To avoid complications, we shall omit the spin variable. Since the above comments hold also for the optimized effective potential approximation (OEP) of UHF, we shall consider this approximation for simplicity, considering that the radial parts of the orbitals are obtained by solving a Schrödinger type one-particle equation

$$-\frac{1}{2} \frac{d^2}{dr^2}u^l_n(r) + \frac{l(l+1)}{2r^2}u^l_n(r) + V_{ef}(r)u^l_n(r) = \epsilon^l_n u^l_n(r)$$

(20)

restricting the effective potential $V_{ef}(r)$ to those having spherical symmetry. The orbitals are of the form

$$\phi^l_{n,m}(r,v) = \frac{u^l_n(r,v)}{r}Y_m(\theta,\varphi)$$

(21)

where the first suffix denotes the energy levels $\epsilon^l_n$ for fixed $l$ in ascending order.

The next step is to construct the Slater determinant with fixed $L_z$. As an example we take the three particle case with $L_z$ eigenvalue equal to 0.

$$|\Phi(v) > = |\phi^0_{1,0},\phi^1_{1,-1},2;1,1 > .$$

(22)

The next step is to minimize $\langle \Phi(V_{ef})|H|\Phi(V_{ef}) >$ with respect to the effective potential $V_{ef}(r)$. After the effective potential and the orbitals are determined, one analyzes $|\phi^0_{1,0},\phi^1_{1,-1},2;1,1 >$ in eigenstates of $L^2$. Then, after rejecting the first suffix for convenience, we have

$$|\phi^0_{1,0},\phi^1_{1,-1},2;1,1 > = |1,0|1,-1;2,1 > |\Psi^0 > + |2,0|1,-1;2,1 > |\Psi^0 >$$

$$+ |3,0|1,-1;2,1 > |\Psi^0 >$$

(23)

where the $|l,m|l_1,m_1;l_2,m_2 >$ are Clebsch-Gordan coefficients.

As an example, we shall calculate the corrected energy $E^1$ of $|\Psi^0 >$, the explicit form of which is

$$|\Psi^0 > = \frac{1}{\sqrt{10}} \{ \sqrt{3}|\phi^0_{0,0},\phi^1_{1,1} > - |\phi^0_{0,0},\phi^1_{1,1} > - |\phi^0_{0,0},\phi^1_{1,1} > + \sqrt{3}|\phi^0_{0,0},\phi^1_{1,1} > \}$$

(24)

In calculating the energy $E^1 = \langle \Psi^0 |H|\Psi^0 >$, one must take into account that the kinetic and external potential terms have only diagonal elements since they are one-particle operators and the Sladets of the expansion differ by two particles. Thus e.g. $\langle \phi^0_{0,0},\phi^1_{1,1}|T|\phi^0_{0,0},\phi^1_{1,1} > = 0$. Further,

$$\langle \phi^0_{0,0},\phi^1_{1,1}|T|\phi^0_{0,0},\phi^1_{1,1} > = \langle \phi^0_{0,0},\phi^1_{1,1}|T|\phi^0_{0,0},\phi^1_{1,1} > = \sum_{l=0}^{2} \langle \phi^l_{m}|T|\phi^l_{m} >$$

(25)
and in general the kinetic energy does not depend on the lower indices of the orbitals since by applying the $L^+$ successively we can go from the lower to the higher eigenvalues of $L_z$. Thus

$$<\varphi^l_{m+1}|T|\varphi^l_{m+1}> = c <L^+\varphi^l_m|T|L^+\varphi^l_m> = c <\varphi^l_m|T|L^-L^+\varphi^l_m> = <\varphi^l_m|T|\varphi^l_m>. \quad (26)$$

Thus the diagonal terms will give the same energy as the minimizing state $|\Phi>$. Then,

$$E^l = <\Psi^l_0|H|\Psi^l_0> - \frac{1}{\sqrt{10}} \{2\sqrt{3} <\varphi^0_0,\varphi^1_1,\varphi^2_{-1}|H_{int}|\varphi^0_0,\varphi^1_1,\varphi^2_{-1}> + 2\sqrt{3} <\varphi^0_0,\varphi^1_1,\varphi^0_{-1}|H_{int}|\varphi^0_0,\varphi^1_1,\varphi^0_{-1}> + 3 <\varphi^0_0,\varphi^1_1,\varphi^2_{-1}|H_{int}|\varphi^0_0,\varphi^1_1,\varphi^2_{-1}> + c.c. \} \quad (27)$$

The off diagonal terms are of the form $<\varphi^0_0\varphi^1_1|H_{int}|\varphi^0_0\varphi^1_1>$. The explicit form of these matrix elements is

$$<\varphi^0_0,\chi_i\chi_j|H_{int}|\varphi^0_0\chi_k\chi_l> = J(\chi_i,\chi_j; \chi_k\chi_l) - J(\chi_i\chi_j; \chi_k\chi_l) \quad (28)$$

where

$$J(\chi_i,\chi_j; \chi_k\chi_l) = \int d^3r \int d^3r' \chi^*_i(r)\chi^*_j(r') \frac{1}{|r-r'|} \chi_k(r)\chi_l(r'). \quad (29)$$

The value of the off-diagonal term gives the correlation energy. This energy, can be positive or negative and there will be at least one $|\Psi^l_0>$ which will have energy less than the one obtained from the unrestricted HF, but we cannot judge, which $l$ gives the smallest energy without doing the actual calculation.

After this example, one can consider the general case of spherical symmetry, following the procedure of the above example. In order to find the $L^2$ eigenstates of the expansion one can act on the Slater state

$$|\Phi_m> = a^{l_1\dagger}_{m_1}...a^{l_n\dagger}_{m_n}|0> \quad (30)$$

expressed as a single product of creation operators, and acting successively with $L^+$ one will get finally a single Slater

$$|\Phi^l_> = a^{l_1\dagger}_{l_1}...a^{l_n\dagger}_{l_n}|0> \quad (31)$$

Next, following the reverse procedure, one will get $|\Phi^l_{-1}> = cL^-|\Phi^l_> >$ and by using orthogonality, can determine $|\Phi^l_{-1}>$. A detailed account of this procedure for the case of spin symmetry is given in [16]. Finally one determines the expansion of $|\Phi_m>$ as a sum the $|\Phi^l_m>$ states by means of which the energy correction is determined.

The procedure is applicable for any symmetry. In each case some simplifications appear. Thus, in the case of the spin symmetry, which is always present in atoms, molecules and solids, one can prove certain theorems which lead to further simplifications. Details of the theory and applications to molecules are given in the paper that follows [14].

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