Approximate spin symmetries in single determinantal approximations of many electron systems

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Abstract. In this paper, we examine the deviation of the minimizing states of the unrestricted Hartree-Fock approximation to those of the restricted one. We find that the deviation is small and so is the spin contamination. We also present numerical results for some molecules. We show that for the $S=0$ case, it is possible to have a class of solutions with high spin contamination.

1. Introduction

A symmetry which is always present in atoms, molecules and solids, when spin-orbit interaction is not included, is spin symmetry, i.e. the Hamiltonian of a many electron system, in the absence of an external magnetic field, is invariant under rotations in the spin space. This is obvious since the Hamiltonian does not contain spin terms. Therefore, the exact eigenstates of these systems are also eigenstates of the total spin operators $S_z$ and $S^2$, where the eigenvalues $S(S+1)$ of $S^2$ characterize the irreducible representations (Irreps) of the spin symmetry. The labelling of the energy eigenstates by $S$ is a property very important not only from the theoretical but also from the experimental point of view, as the application of an external uniform magnetic field $B$ gives a splitting of the $2S+1$ degenerate eigenstates into $2S+1$ energy levels, having energy $E_S^0 - gBM$, where $E_S^0$ is the energy of the exact eigenstate of the Hamiltonian $H$ in zero magnetic field, $g$ is the Landé factor and $M$ is the eigenvalue of $S_z$ which ranges from $-S$ to $S$. In this way, the experimentalist, by varying the strength of the external magnetic field, can derive many properties of the energy eigenstates of the physical system under consideration.

Most quantum mechanical calculations concerning atoms molecules and solids use single Slater determinant (Sladet) approximations as these are simple to implement and have very small computational cost than more accurate approximation theories, which use linear combinations of such determinants. Such single Sladet approximations are the Hartree-Fock (HF), the optimized effective potential (OEP) [1, 2] and density functional theories (DFT) [3, 4].

In applying an approximation theory, one must know its limitations, i.e., one must know which physical properties can be derived with sufficient accuracy and which cannot. Usually, a good approximation to the energy is sought, but other features are also of interest like e.g. the transformation properties and in particular the eigenvalues of experimentally measurable quantities, like e.g. the eigenvalues of $S_z$ and $S^2$. Although considerable theoretical work has been done by March [5, 6, 7, 8], Parr [9, 10, 12], Levy [15, 14], Gross [17, 18] with their coworkers and a long list of other scientists especially in DFT, to our knowledge, no investigations have been carried out in order to determine the relation of the approximate to the exact eigenstate. The interest is usually limited to the comparison of the approximate to the exact ground state.
energy. But, in doing so one gets better energy approximations when symmetry is broken. Thus, the minimizing state of the HF approximation is not an eigenstate of $S^2$, but only an eigenstate of $S_z$, unless one restricts the search for minima in the space of Sladets which are eigenstates of $S^2$. The second case is referred as the restricted HF in contrast to the first which is called unrestricted. Thus it is of interest to find out how near the states of the two calculations are. Measure of this nearness is the overlap of the corresponding wave functions.

Although the above approximation theories were initially introduced for the ground state, they can be applied to the lower energy eigenstates belonging to an irreducible representation (Irrep) of the symmetry group of the Hamiltonian. Thus, instead of searching for the minimum in the whole space of determinants, one can search for the minimum in the subspaces of Sladets of fixed $M$. In this paper we shall deal with the proximity of the states derived by restricted and unrestricted approximations, which is measured by the overlap $|<\Phi_M|\Psi_M>|$ where the $|\Phi_M>$ state is calculated in the space of Sladets which are eigenstates of $S^2$ whereas $|\Psi_M>$ are the minimizing states in the space of Sladets having $S_z = M$. Some numerical calculations showing the deviation from symmetry will be presented.

2. Expansion of a Slater determinant in terms of eigenstates of $S^2$

We shall deal mainly with the Hartree-Fock approximation, since this is the most difficult case because of the non local character of the exchange operator. The HF approximation to the energy of a $N$-electron system with Hamiltonian $H$ and $S_z = M$ is defined as the minimum of the functional

$$ E(\Phi_M) = |<\Phi_M|H|\Phi_M>|, |<\Phi_M|\Phi_M>| = 1. \tag{1} $$

Thus, let us denote by

$$ |\Phi_M> = |\varphi_1^1, \varphi_2^1, \ldots, \varphi_s^l, \varphi_1^{l+1}, \varphi_2^{l+1}, \ldots, \varphi_l^l>, \tag{2} $$

the Sladet with $k$ spin orbitals up and $l$ down, i.e. $|\Phi_M>$ corresponds to the $N = k + l$ electron wave function with $M = (k-l)/2$. The explicit form of $|\Phi_M>$ is

$$ \Phi_M(r_1, s_1, r_2, s_2, \ldots, r_N, s_N) = (N!)^{-1/2} \det[\varphi_i^j(r_j)u_r^s(s_j)], \tag{3} $$

where the index $s$ refers to the spin up and spin down single particle states. For the sake of avoiding many indices, in the following we shall denote by $\varphi_i(r)$ and $\varphi_i^j(r)$ the spatial parts of the spin up and the spin down orbitals, which are orthonormal i.e. $<\varphi_i^s|\varphi_j^t> = \delta_{ij}$, while the $<\varphi_i|\varphi_j^t>$ in general are not equal to 0. The $N$-electron Hamiltonian of an atom, molecule or solid is of the form

$$ H = T + H_{int} + V, $$

where

$$ T = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2, \quad H_{int} = \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{|r_i - r_j|}, \quad V = \sum_{i=1}^{N} V(r_i). \tag{4} $$

Then, the energy corresponding to a Slater determinant $|\Phi_M>$ is $E(\Phi_M) = |<\Phi_M|H|\Phi_M>|$

$$ E(\Phi_M) = |<\Phi_M|T|\Phi_M>| + |<\Phi_M|H_{int}|\Phi_M>| + |<\Phi_M|V|\Phi_M>| $$

By applying the minimization procedure for $E(\Phi_M)$ one gets the Hartree-Fock equations for the spin up and spin down orbitals,

$$ [-\frac{1}{2} \nabla^2 + V(r)]\varphi_i^s(r) + \int d^3r'\frac{\rho_F(r')}{|r' - r|}\varphi_i^s(r') - \int d^3r'\frac{\rho_F^s(r', r')}{|r' - r|}\varphi_i^s(r') = \epsilon_i^s \varphi_i^s(r), \tag{5} $$
where
\[ \rho_k^m(r) = \rho_k^m(r, r), \rho_k(r) = \rho_k^m(r) + \rho_k^m(r), \]
\[ \rho_k^m(r, r') = \langle \Phi_k|\hat{\rho}_m(r, r')|\Phi_k \rangle = \langle \Phi_k|\hat{\psi}^m(r)\hat{\psi}^m(r')|\Phi_k \rangle, \]
and \( \hat{\psi}^m(r), \hat{\psi}^m(r') \) are the field creation and annihilation operators. The spin up exchange term is different from the spin down one when \( k \neq l \), since if we assume \( \rho_k^m(r, r') = \rho_k^m(r, r') \), then \( \rho_k^m(r) = \rho_k^m(r) \), but this is not possible since \( \int d^3r \rho_k^m(r) = k \), \( \int d^3r \rho_k^m(r) = l \), while equality requires \( k = l \). Thus in general \( \varphi_i(r) \neq \varphi_i'(r) \). So, it is not possible for the spatial parts of the up and down orbitals to coincide. Let us assume that it is possible for some of them to coincide, e.g. \( \varphi_m(r) = \varphi'_m(r) \). Then by subtracting the spin up and spin down equation for \( i = m \), we find
\[ \int d^3r \rho_k^m(r, r') = \rho_k^m(r, r') \]
\[ \varphi_m(r') = (e_m - e_m')\varphi_m(r), \quad (6) \]

It is a strong condition since the explicit form of the density matrices is \( \rho_k^m(r, r') = \sum_{i = 1}^k \varphi_i^m(r)\varphi_i^m(r') \). Thus in general
\[ \varphi_i(r) \neq \varphi_i'(r) \]

In the following we shall consider \( l \leq k \) for convenience.

In order to find the overlap of the minimizing state \( |\Phi_M \rangle \) with a \( |\Phi_S^k \rangle \) state it is necessary to express it as a sum of eigenstates of \( S^2 \). But this is possible when the spatial parts of the spin orbitals are either doubly occupied or orthogonal, since for this case we have a formula for the expansion coefficients[28]. The proof is simplified if we use creation and annihilation operators \( \hat{a}_i^\dagger, \hat{a}_i^\dagger \) for the spin orbitals \( \varphi_i^k \) whose spatial parts are mutually orthogonal. Then a Sladet \( |\Theta_{M,J,k',\ell'} \rangle \) with \( J \) orbitals doubly occupied, \( k' \) up and \( \ell' \) down, and \( M = k' - \ell' \), can be expressed as a product of creation operators acting on the vacuum state \( |0 \rangle \),
\[ |\Theta_{M,J,k',\ell'} \rangle = \hat{a}_1^\dagger \hat{a}_1^\dagger \ldots \hat{a}_j^\dagger \hat{a}_j^\dagger \hat{a}_{j+1}^\dagger \ldots \hat{a}_{k'}^\dagger \hat{a}_{k'}^\dagger \hat{a}_{j+1}^\dagger \ldots \hat{a}_{k'-1}^\dagger |0 \rangle. \quad (7) \]

The product of these operators can be expressed as a product of three irreducible tensor operators (IrTeO) acting on the vacuum state, i.e.,
\[ |\Theta_{M,J,k',\ell'} \rangle = A_{M,J,k',\ell'}^0 \hat{A}_{k',\ell'}^0 |0 \rangle. \quad (8) \]

We must now expand \( |\varphi_i^k \rangle \) as a linear combination of \( |\varphi_i \rangle \), of the subspace \( S_k \), and \( |\varphi_{i+k} \rangle \) orthogonal to \( S_k \). This would result to the expansion of \( |\Phi_M \rangle \) in a sum of many Sladets. Fortunately, many simplifications result by using Theorem 1, proved in[29]

**Theorem 1.** If \( S_k \) and \( S_l \) are subspaces of an inner product space of dimension \( k \) and \( l \) respectively and \( k \geq l \) then an orthonormal basis \( |\varphi_i \rangle \) exists in \( S_k \) so that the basis vectors \( |\varphi_i^k \rangle \) of \( S_l \) can be expressed as
\[ |\varphi_i^k \rangle = c_i |\varphi_i \rangle + c_{i+k} |\varphi_{i+k} \rangle, \quad (9) \]

with \( < \varphi_i | \varphi_{j+k} > = \delta_{ij} \) and \( < \varphi_{i+k} | \varphi_{j+k} > = \delta_{ij} \) for \( i = 1, \ldots, k \) and \( j = 1, \ldots, l \).

From the above theorem follows directly

**Theorem 2.** Any Sladet with \( k \) spin orbitals up and \( l \) down can be expressed as
Table 1. Energies (in hartree) of symmetry preserving and symmetry breaking states $|\Phi_M^M\rangle$ and $|\Phi_M\rangle$

| System         | $E(\Phi_M^M)$ | $E(\Phi_M)$ | $\Delta E$ |
|----------------|---------------|-------------|------------|
| Li($^2S$)     | -7.43180      | -7.43182    | 0.02       |
| B($^2P$)      | -24.52636     | -24.52637   | 0.38       |
| C($^3P$)      | -37.68316     | -37.68415   | 0.99       |
| N($^4S$)      | -54.39433     | -54.39679   | 2.46       |
| O($^3P$)      | -74.80130     | -74.80423   | 2.93       |
| F($^2P$)      | -99.39987     | -99.40095   | 1.08       |
| BeH($^2\Sigma^+$) | -15.14428    | -15.14479   | 0.51       |
| CH($^2\Pi$)   | -38.27080     | -38.27174   | 0.94       |
| NH($^3\Sigma^-$) | -54.96453    | -54.96912   | 4.59       |
| CH$_2$(3$^1B_1$) | -38.91970    | -38.92319   | 3.49       |
| NH$_2$(2$^1B_1$) | -55.57068    | -55.57246   | 1.78       |

Table 2. Spin contamination $S_{\text{con}}$ and overlap $|<\Phi_M|\Phi_M^M>|$ for various molecules

| System         | $S_{\text{con}}$ | $|<\Phi_M|\Phi_M^M>|$ |
|----------------|------------------|----------------------|
| Li($^2S$)     | 0.00001          | 0.99999              |
| B($^2P$)      | 0.00115          | 0.89473              |
| C($^3P$)      | 0.00172          | 0.95888              |
| N($^4S$)      | 0.00305          | 0.99861              |
| O($^3P$)      | 0.00542          | 0.97912              |
| F($^2P$)      | 0.00220          | 0.93892              |
| BeH($^2\Sigma^+$) | 0.00117        | 0.99950              |
| CH($^2\Pi$)   | 0.00401          | 0.89832              |
| NH($^3\Sigma^-$) | 0.01339        | 0.99504              |
| CH$_2$(3$^1B_1$) | 0.00838        | 0.99657              |
| NH$_2$(2$^1B_1$) | 0.00708        | 0.99780              |

$|\Phi_M\rangle = |\varphi_1^\uparrow, \varphi_2^\uparrow, ..., \varphi_k^\uparrow, c_1\varphi_1^\downarrow + c_{1+k}\varphi_{1+k}^\downarrow, ..., c_i\varphi_i^\downarrow + c_{i+k}\varphi_{i+k}^\downarrow, ..., c_l\varphi_l^\downarrow + c_{l+k}\varphi_{l+k}^\downarrow, ...\rangle$, \hspace{1cm} (10)

where the spatial orbitals are mutually orthogonal.

Theorem 2 is a consequence of the fact that a Sladet is a mapping of an N-dimensional space to a vector in the space of N spatial variables. This mapping is antisymmetric and linear with respect to each of its arguments. Hence it is a determinant.

In this paper we present our numerical results with the minimising states $|\Phi_M\rangle$ and $|\Phi_M^M\rangle$ calculated by the direct mapping theory. As one can easily conclude from Tables 1 and 2 the symmetry breaking of the unrestricted HF is small. A measure of this symmetry breaking is the spin contamination $S_{\text{con}},$

$$S_{\text{con}} = <\Phi_M|S^2|\Phi_M> - M(M + 1).$$ \hspace{1cm} (11)
The calculations were done by applying the direct mapping theory\cite{30}, \cite{31}, with optimized effective potential

\[ V(r) = \sum_k Z_k \frac{Z_k}{|r - R_k|} \{ -1 + \frac{(N - 1)C^a}{Z} [1 - \exp(-Z_k^\delta |r - R_k|)] \}, \]

where the parameters \( C^a \) and \( Z_k^\delta \) are determined from the minimization of the energy \( E(\Phi_M) \).

In the next section we shall give another aspect of the HF theory, by defining functionals on two Sladets.

3. HF by means of two Sladet functionals

The kinetic energy term is

\[ < \Phi_M | T | \Phi_M > = \frac{1}{2} \int d^3r \sum_{i=1}^k |\nabla \varphi_i(r)|^2 + \frac{1}{2} \int d^3r \sum_{i=1}^l |\nabla \varphi'_i(r)|^2. \]

Thus it can be expressed as a sum of two terms

\[ < \Phi_M | T | \Phi_M > = < \Phi_k | T | \Phi_k > + < \Phi_l | T | \Phi_l >, \]

where

\[ < \Phi_k | T | \Phi_k > = \frac{1}{2} \int d^3r \sum_{i=1}^k |\nabla \varphi_i(r)|^2, \]

\[ < \Phi_l | T | \Phi_l > = \frac{1}{2} \int d^3r \sum_{i=1}^l |\nabla \varphi'_i(r)|^2, \]

and

\[ |\Phi_k > = |\varphi_1, \varphi_2, ..., \varphi_k >, \]

\[ |\Phi_l > = |\varphi'_1, \varphi'_2, ..., \varphi'_l >. \]

In the same way the external potential term is

\[ < \Phi_M | V | \Phi_M > = < \Phi_k | V | \Phi_k > + < \Phi_l | V | \Phi_l >. \]

The exchange part of the interaction energy can also be separated in two terms, \( E_x(\Phi_k), E_x(\Phi_l) \),

\[ E_x(\Phi_q) = -\frac{1}{2} \int d^3r \int d^3r' \frac{e^2}{|r - r'|} \rho_q(r, r') \rho_q(r', r), \]

where

\[ \rho_k(r, r') = \sum_{i=1}^k \varphi^*_i(r) \varphi_i(r'), \]

\[ \rho_l(r, r') = \sum_{i=1}^l \varphi'^*_i(r) \varphi'_i(r'). \]

The only term which involves products of functionals of \( |\Phi_k > \) and \( |\Phi_l > \) is the Hartree term of the interaction energy \( |\Phi_M > \),

\[ E_h(\Phi_M) = \frac{1}{2} \int d^3r \int d^3r' \frac{e^2}{|r - r'|} [\rho_k(r) + \rho_l(r)] [\rho_k(r') + \rho_l(r')]. \]
Thus $< \Phi_M | H | \Phi_M >$ is a functional $E(\Phi_k, \Phi_l)$ of the Slater determinants $| \Phi_k >$ and $| \Phi_l >$

$$E(\Phi_k, \Phi_l) = E(\Phi_k) + E(\Phi_l) + \int d^3r \int d^3r' \frac{e^2}{|r - r'|} \rho_k(r) \rho_l(r'),$$  

(17)

where

$$E(\Phi_q) = < \Phi_q | T + V | \Phi_q > + E_x(\Phi_q) + \frac{1}{2} \int d^3r \int d^3r' \frac{e^2}{|r - r'|} \rho_q(r) \rho_q(r').$$  

(18)

From the above expression it is obvious that we can apply the variational principle separately for $| \Phi_k >$ and $| \Phi_l >$ for finding the extrema of $E(\Phi_k, \Phi_l)$. The resulting equations are

$$(T + V) | \Phi_k > + \tilde{V}_x(\Phi_k) | \Phi_k > + \tilde{V}_h(\Phi_k, \Phi_l) | \Phi_k > = E_k | \Phi_k >,$$

(19)

and

$$(T + V) | \Phi_l > + \tilde{V}_x(\Phi_l) | \Phi_l > + \tilde{V}_h(\Phi_k, \Phi_l) | \Phi_l > = E_l | \Phi_l >, $$

(20)

where

$$\tilde{V}_x(\Phi_q) = - \int d^3r d^3r' \frac{e^2}{|r - r'|} \rho(r, r') < \Phi_q | \tilde{\rho}(r', r) | \Phi_q >,$$

(21)

where $\tilde{\rho}(r, r') = \tilde{\psi}^\dagger(r) \tilde{\psi}(r')$ and $\tilde{\psi}(r), \tilde{\psi}(r')$ are the field creation and field annihilation operators for fermions.

For the case $k = l$ let us denote the Slater determinant with the spin up orbitals with $| \Phi_k >$ and that with the spin down with $| \Phi_k' >$. Then by taking scalar products of both sides of the above equations with $| \Phi_k' >$ and $| \Phi_k >$ respectively, we find

$$< \Phi_k' | (T + V) | \Phi_k > + < \Phi_k' | \tilde{V}_x(\Phi_k) | \Phi_k > + < \Phi_k' | \tilde{V}_h(\Phi_k, \Phi_k') | \Phi_k > = E_k < \Phi_k' | \Phi_k >, $$

(22)

and

$$< \Phi_k | (T + V) | \Phi_k' > + < \Phi_k | \tilde{V}_x(\Phi_k') | \Phi_k' > + < \Phi_k | \tilde{V}_h(\Phi_k, \Phi_k') | \Phi_k' > = E_k < \Phi_k | \Phi_k' >. $$

(23)

By taking complex conjugate of the second equation, after taking into account the hermiticity of all operators involved, we have

$$< \Phi_k' | (T + V) | \Phi_k > + < \Phi_k' | \tilde{V}_x(\Phi_k') | \Phi_k > + < \Phi_k' | \tilde{V}_h(\Phi_k, \Phi_k') | \Phi_k > = E_k' < \Phi_k' | \Phi_k >. $$

(24)

By subtracting Eq. (22) from Eq. (22) we are left with the equation

$$< \Phi_k' | \tilde{V}_x(\Phi_k) | \Phi_k > - < \Phi_k | \tilde{V}_x(\Phi_k') | \Phi_k' > = (E_k - E_k') < \Phi_k' | \Phi_k >. $$

(25)

By introducing the explicit forms of $\tilde{V}_x(\Phi_q)$ the left hand side becomes

$$- < \Phi_k | \int d^3r \int d^3r' \frac{e^2}{|r - r'|} \tilde{\rho}(r, r') < \Phi_k | \tilde{\rho}(r', r) | \Phi_k > | \Phi_k > +$$

$$< \Phi_k | \int d^3r \int d^3r' \frac{e^2}{|r - r'|} \tilde{\rho}(r, r') < \Phi_k | \tilde{\rho}(r', r) | \Phi_k' > | \Phi_k' > =$$
\[- \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} < \Phi_k^\prime | \tilde{\rho}(\mathbf{r}, \mathbf{r}') | \Phi_k > [ < \Phi_k | \tilde{\rho}(\mathbf{r}', \mathbf{r}) | \Phi_k > - < \Phi_k^\prime | \tilde{\rho}(\mathbf{r}', \mathbf{r}) | \Phi_k^\prime > ]. \quad (26)\]

Thus finally we get the relation

\[- \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} < \Phi_k^\prime | \tilde{\rho}(\mathbf{r}, \mathbf{r}') | \Phi_k > [ < \Phi_k | \tilde{\rho}(\mathbf{r}', \mathbf{r}) | \Phi_k > - < \Phi_k^\prime | \tilde{\rho}(\mathbf{r}', \mathbf{r}) | \Phi_k^\prime > ] = (E_k - E_k^\prime) < \Phi_k^\prime | \Phi_k > . \quad (27)\]

Thus every solution has to satisfy the above condition. This means that one type of solutions is that with \(|\Phi_k^\prime> = \Phi_k>\) and therefore \(E_k = E_k^\prime\) and \(< \Phi_k | \tilde{\rho}(\mathbf{r}', \mathbf{r}) | \Phi_k > = < \Phi_k^\prime | \tilde{\rho}(\mathbf{r}', \mathbf{r}) | \Phi_k^\prime >\).  The other extreme case is that where \(< \Phi_k^\prime | \Phi_k > = 0\). This situation is trivially realized when \(\Phi_k >\) and \(\Phi_k^\prime >\) differ by two orbitals. Then, \(< \Phi_k^\prime | \tilde{\rho}(\mathbf{r}, \mathbf{r}') | \Phi_k > = 0\) since \(\tilde{\rho}(\mathbf{r}, \mathbf{r}')\) is a one-particle operator.

4. Conclusions

With the above procedure we conclude that the unrestricted HF for \(M = 0\) has two qualitatively different stable solutions. The first one is an eigenstate of \(S^2\) with eigenvalue 0 while the second one presents high spin contamination. It is of interest to find out the nature of the solutions for \(M > 0\). The problem is not easy as one has to do with the case that \(\Phi_k >\) and \(\Phi_k^\prime >\) are of different dimension and thus one cannot take scalar products. All present day calculations on spin contamination suggest that the small spin contamination is the rule and the large one the exception. However, in applying a numerical procedure in such calculations, one may slip from the one case to the other and this may lead to failure of convergence and the production of results which are not in agreement with physical reality.

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