

A generalized self-consistent-field procedure in the improved BCS theory

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The basic ideas of the Improved Bardeen–Cooper–Schrieffer (IBCS) approach to the first- and second-order Reduced Density Matrices (1- and 2-RDM) are briefly reviewed. The molecular orbital occupations $\{\rho_q\}$ are expressed by means of new quantities $\{\gamma_q\}$, which, satisfying a trigonometric relation, guarantee the non-idempotent condition. Thus, a variational method is introduced to determine $\{\rho_q\}$, involving only an unconstrained minimization which may be performed using a conjugate gradient technique. A new effective Hamiltonian \hat{V} which is composed of the Coulomb, exchange and exchange-time inversion operators is also presented. It leads exactly to equations of Hartree–Fock type, however, the electronic field includes now an arbitrary number of orbitals and fractional occupation numbers. Accordingly, a generalized self-consistent-field method is proposed: the iterative procedure is repeated until convergence is reached for the actual density matrix.

1. Introduction

Recently, we have proposed the Improved Bardeen–Cooper–Schrieffer (IBCS) approximation for taking into account the electron correlation in molecules with a large number of electrons [7–9].

In these previous papers, we developed our method within the framework of the Reduced Density Matrix (RDM) formalism, introduced a new exchange and time inversion operator for considering electron correlation, and provided the first derivatives of the IBCS total energy with respect to nuclear coordinates. The basic ideas of our approach to the RDM are briefly reviewed in section 2.

Up to now, the IBCS set of equations was solved using a constrained optimization algorithm. In this paper, a new approach which only involves unconstrained minimization is proposed. This is done in section 3, by expressing the usual BCS variational parameters $\{P_q\}$ and $\{\Phi_q\}$, hence the occupations $\{\rho_q\}$, via new quantities $\{\gamma_q\}$ which, satisfying a trigonometric relation, assure the relations between old elements. Thus, the minimization may be performed using conjugate gradients [10] or other standard techniques. The success of the conjugate gradient minimization has been recently

demonstrated by Li et al. [3], Millan and Scuseria [5], who have proposed a density matrix search method at the Hartree–Fock (HF) level.

On the other hand, in the IBCS method the molecular basis must diagonalize the one-particle RDM (1-RDM), so we should refine the basis. As obtained in [9], this leads to the one-particle operator \widehat{V}_q which determines a new set of molecular orbitals, including electron correlation. Because of the dependence on q , a different operator always creates different orbitals, and, consequently, we cannot try this problem as a pseudo eigenvector–eigenvalue problem. In section 4 of this article, we focus our attention on modifying operator \widehat{V}_q and present a new generalized Fock operator \widehat{V} . The energy expression and the set of equations which now define molecular orbitals look exactly the same as those of an independent particle HF model theory.

As a result, a search over all possible $\{\rho_q\}$ and the associated orthonormal orbitals $\{|q\rangle\}$ is proposed. This idea is similar to the one due to Janak [2] of a more general Kohn–Sham (KS) Density Functional Theory (DFT), where the ground-state energy is also obtained by minimizing $E[\rho]$ with respect to the occupations and the one-particle functions $\{\psi_q\}$. However, the Janak effective potential is different from the one obtained in this paper, since the former does not depend on the occupations. As it was demonstrated by Perdew and Zunger [6], there is a non-trivial problem concerning the inference of which distribution of $\{\rho_q\}$ minimizes the total energy. Moreover, there may be systems for which Janak’s method does not work. In order to overcome this problem, a more general theory is developed here.

2. The IBCS reduced density matrices

The electronic energy for a system with a number N_e of electrons is given by the expression [9]

$$E_e = \sum_{q,\sigma,q',\sigma'} \langle q\sigma | \widehat{h} | q'\sigma' \rangle^1 d_{q'\sigma';q\sigma} + \sum_{q_1,\sigma_1,q_2,\sigma_2,q'_1,\sigma'_1,q'_2,\sigma'_2} \langle q_1\sigma_1, q_2\sigma_2 | q'_1\sigma'_1, q'_2\sigma'_2 \rangle^2 d_{q'_1\sigma'_1,q'_2\sigma'_2;q_1\sigma_1,q_2\sigma_2}, \quad (1)$$

in which $\langle q\sigma | \widehat{h} | q'\sigma' \rangle$ is the matrix element ($q\sigma, q'\sigma'$) of the kinetic energy and nuclear attraction terms (one-electron operator \widehat{h}), and $\langle q_1\sigma_1, q_2\sigma_2 | q'_1\sigma'_1, q'_2\sigma'_2 \rangle$ are the electronic repulsion integrals. The states $|q\sigma\rangle$ constitute a complete *orthonormal* set of single-particle wave functions, i.e.,

$$\langle q'\sigma' | q\sigma \rangle = \delta_{q',q} \delta_{\sigma',\sigma}, \quad (2)$$

where q denotes the orbital and σ is the sign of the spin projection (it takes two values $+1$ and -1). The matrices ${}^1d_{q'\sigma';q\sigma}$ and ${}^2d_{q'_1\sigma'_1,q'_2\sigma'_2;q_1\sigma_1,q_2\sigma_2}$ are the 1-RDM and the 2-RDM, respectively, both in the $(q\sigma)$ -representation.

In the IBCS method, the 2-RDM of a *large* system with an even number of electrons is approximated by the BCS 2-RDM, i.e.,

$$\begin{aligned} {}^2d_{q'_1\sigma'_1, q'_2\sigma'_2; q_1\sigma_1, q_2\sigma_2} &= \frac{1}{2} \langle \Psi_{\text{BCS}} | a_{q_1\sigma_1}^\dagger a_{q_2\sigma_2}^\dagger a_{q'_2\sigma'_2} a_{q'_1\sigma'_1} | \Psi_{\text{BCS}} \rangle \\ &= \frac{1}{2} (P_{q'_1\sigma'_1; q_1\sigma_1} P_{q'_2\sigma'_2; q_2\sigma_2} - P_{q'_1\sigma'_1; q_2\sigma_2} P_{q'_2\sigma'_2; q_1\sigma_1} \\ &\quad + \Phi_{q'_2\sigma'_2; q'_1\sigma'_1} \Phi_{q_2\sigma_2; q_1\sigma_1}), \end{aligned} \quad (3)$$

in which

$$P_{q'\sigma'; q\sigma} = P_q \delta_{q, q'} \delta_{\sigma, \sigma'}, \quad (4)$$

$$\Phi_{q'\sigma'; q\sigma} = \sigma \Phi_q \delta_{q, q'} \delta_{\sigma, -\sigma'}, \quad (5)$$

$$P_q = P_q^2 + \Phi_q^2. \quad (6)$$

On the other hand, the 1-RDM is obtained by contraction of the 2-RDM,

$${}^1d_{q'\sigma'; q\sigma} = \frac{2}{N_e - 1} \sum_{i,s} {}^2d_{q'\sigma'; i,s; q\sigma, i,s} = \rho_q \delta_{q', q} \delta_{\sigma', \sigma}, \quad (7)$$

$$\rho_q = \frac{S - 1}{N_e - 1} P_q + \frac{2\Phi_q^2}{N_e - 1}, \quad S = 2 \sum_q P_q, \quad (8)$$

and it is compelled to obey the trace condition:

$$\sum_{q,\sigma} {}^1d_{q\sigma; q\sigma} = \frac{S - 1}{N_e - 1} S + \frac{4 \sum_q \Phi_q^2}{N_e - 1} = N_e. \quad (9)$$

This improvement guarantees the particle number conservation. In fact, the mean value of the particle number operator, $\langle \widehat{N} \rangle$, will be equal to N_e , and, if we take as a measure of non-conservation the standard deviation of the particle number operator, we obtain that it is exactly equal to zero:

$$\begin{aligned} D &= \langle \widehat{N}^2 \rangle - \langle \widehat{N} \rangle^2 \\ &= \sum_{q,\sigma} {}^2d_{q\sigma; q\sigma} + 2 \sum_{q,\sigma, q', \sigma'} {}^2d_{q\sigma, q'\sigma'; q\sigma, q'\sigma'} - \left(\sum_{q,\sigma} {}^1d_{q\sigma; q\sigma} \right)^2 = 0. \end{aligned} \quad (10)$$

The next step is to consider that N_e is a large value, therefore, we can neglect the second term in equation (9) and take $S = N_e$. Since the matrix $\langle q\sigma | \widehat{h} | q'\sigma' \rangle$ depends on N_e , we have to consider all the terms for evaluating the total energy. By substitution of the density matrices into equation (1) we get, finally,

$$\begin{aligned}
E_e = & \sum_{q,\sigma} \langle q\sigma | \hat{h} | q\sigma \rangle \rho_q + \frac{1}{2} \sum_{q,\sigma,q',\sigma'} \langle q\sigma, q'\sigma' | q\sigma, q'\sigma' \rangle P_q P_{q'} \\
& - \frac{1}{2} \sum_{q,\sigma,q',\sigma'} \langle q\sigma, q'\sigma' | q'\sigma', q\sigma \rangle P_q P_{q'} \\
& + \frac{1}{2} \sum_{q,\sigma,q',\sigma'} \langle q, \sigma; q, -\sigma | q', \sigma'; q', -\sigma' \rangle \sigma\sigma' \Phi_q \Phi_{q'}. \quad (11)
\end{aligned}$$

In this equation, the first term is the sum of the electron kinetic and electron–nuclei potential energies. It can be seen that the electron correlation modifies this term directly, since the value of ρ_q may now be fractional. The second term is the well-known sum of the energies acquired by electrons in the average Coulombic potential field due to all the other electrons. The last two terms are due to the correlation of the electrons through their Coulombic interactions. The former is the well-known exchange energy and the latter is a new energy that adjusts the correlation of particles with anti-parallel spins, it was called the exchange and time inversion energy.

3. Unconstrained minimization

We now look for the elements P_q and Φ_q that minimize the functional (11). These elements must satisfy the non-idempotent constrained condition (6). Equation (6) can be written in a more suitable form:

$$(2P_q - 1)^2 + (2\Phi_q)^2 = 1. \quad (12)$$

Taking advantage of the trigonometric relation

$$\sin^2 \gamma_q + \cos^2 \gamma_q = 1, \quad (13)$$

we can express the original P_q and Φ_q through the new γ_q elements, consequently,

$$P_q = \frac{\sin \gamma_q + 1}{2}, \quad \Phi_q = \frac{\cos \gamma_q}{2}, \quad (14)$$

and the electronic energy, equation (11), will be

$$\begin{aligned}
E_e = & \sum_q \langle q | \hat{h} | q \rangle \left[1 + \sin \gamma_q + \frac{\cos^2 \gamma_q}{N_e - 1} \right] + \frac{1}{2} \sum_{q,q'} \langle qq' | qq' \rangle (\sin \gamma_q + 1)(\sin \gamma_{q'} + 1) \\
& - \frac{1}{4} \sum_{q,q'} \langle qq' | q'q \rangle (\sin \gamma_q + 1)(\sin \gamma_{q'} + 1) + \frac{1}{4} \sum_{q,q'} \langle qq | q'q' \rangle \cos \gamma_q \cos \gamma_{q'}. \quad (15)
\end{aligned}$$

Thus, we could just minimize equation (15) with respect to the new elements γ_q subject to the constraint of fixed N_e . This latter condition in terms of γ_q is expressed as

$$\sum_q (\sin \gamma_q + 1) = N_e. \quad (16)$$

Actually, it would be more convenient to work at fixed chemical potential χ and minimize the grand potential

$$\Omega = E_e - \chi \sum_q (\sin \gamma_q + 1), \quad (17)$$

thereby eliminating the constraint on N_e .

Hence, we have obtained a very simple approach. The grand potential $\Omega(\gamma_q)$ can be minimized using standard off-the-shelf optimization algorithms. We propose to choose the conjugate gradient algorithm, since it only requires the value of the function and its gradients. These gradients are

$$\begin{aligned} \frac{\delta \Omega}{\delta \gamma_q} = & \left[\left(1 - \frac{2 \sin \gamma_q}{N_e - 1} \right) \langle q | \hat{h} | q \rangle - \chi \right] \cos \gamma_q \\ & + \frac{\cos \gamma_q}{2} \sum_{q'} [2 \langle qq' | qq' \rangle - \langle qq' | q'q \rangle] (\sin \gamma_{q'} + 1) \\ & - \frac{\sin \gamma_q}{2} \sum_{q'} \langle qq | q'q' \rangle \cos \gamma_{q'}. \end{aligned} \quad (18)$$

With respect to the chemical potential χ , we require to update its value to enforce the correct number of electrons.

4. The effective Hamiltonian

The IBCS approach is basis-dependent and we should optimize to the utmost the molecular-orbital basis to be used. The variation with respect to $\langle q\sigma |$ regarding the orthonormal condition, equation (2), leads to the equation [9]

$$\hat{V}_q(1) |q\sigma\rangle = \varepsilon_q |q\sigma\rangle, \quad (19)$$

in which $\hat{V}_q(1)$ is a one-particle operator:

$$\hat{V}_q(1) = \rho_q \hat{h}(1) + P_q \sum_{q', \sigma'} [\hat{J}_{q'\sigma'}(1) - \hat{K}_{q'\sigma'}(1)] + \Phi_q \sum_{q', \sigma'} \hat{L}_{q'\sigma'}(1). \quad (20)$$

$\hat{J}_{q\sigma}(1)$ and $\hat{K}_{q\sigma}(1)$ are the usual Coulomb and exchange operators, respectively, and the operator $\hat{L}_{q\sigma}(1)$ is the *exchange-time inversion operator*:

$$\hat{L}_{q\sigma}(1) = \langle q\sigma | \hat{I}^\dagger(2) r_{12}^{-1} \hat{I}(2) \hat{P}_{12} | q\sigma \rangle \Phi_q. \quad (21)$$

The \hat{P}_{12} operator permutes electrons 1 and 2 and the time inversion antiunitary operator $\hat{I}(2)$ changes a ket vector into a bra vector and σ into $-\sigma$, i.e.,

$$\hat{I} |q, \sigma\rangle = \langle q, -\sigma | \sigma. \quad (22)$$

We should keep in mind that we are working with restricted spin-orbitals, and, as a consequence, spin-orbitals energies coincide for both α and β orbitals, that is,

$$\varepsilon_{q+} = \varepsilon_{q-} = \varepsilon_q. \quad (23)$$

Besides, it is important to note that the operator $\widehat{V}_q(1)$ depends on q , therefore a different operator always acts on different spin-orbitals.

Let us now define the one-particle density operator $\widehat{\rho}$ and the two new operators, \widehat{P} and $\widehat{\Phi}$, by means of

$$\widehat{\rho}|q\sigma\rangle = \rho_q|q\sigma\rangle, \quad \widehat{P}|q\sigma\rangle = P_q|q\sigma\rangle, \quad \widehat{\Phi}|q\sigma\rangle = \Phi_q|q\sigma\rangle. \quad (24)$$

They must evidently satisfy the relation

$$\widehat{\rho} = \widehat{P} + \frac{2(\widehat{\Phi})^2}{N_e - 1}. \quad (25)$$

Taking into account these operators we may eliminate the dependence on q and introduce the generalized Fock operator or effective Hamiltonian \widehat{V} as

$$\widehat{V} = \widehat{h}\widehat{\rho} + \sum_{q',\sigma'} [\widehat{J}_{q'\sigma'} - \widehat{K}_{q'\sigma'}] \widehat{P} + \sum_{q',\sigma'} \widehat{L}_{q'\sigma'} \widehat{\Phi}. \quad (26)$$

Equation (19) becomes

$$\widehat{V}(1)|q\sigma\rangle = \varepsilon_q|q\sigma\rangle. \quad (27)$$

In summary, IBCS theory can be conceived as a method where a generalized Fock operator \widehat{V} is used to define a set of molecular orbitals with its corresponding orbital energies. The energy expression, which now includes the correlation effects, looks exactly the same as that of an independent particle HF approximation:

$$E_e = \frac{1}{2} \sum_{q\sigma} [\langle q\sigma|\widehat{h}|q\sigma\rangle\rho_q + \langle q\sigma|\widehat{V}|q\sigma\rangle] = \sum_q [\langle q|\widehat{h}|q\rangle\rho_q + \varepsilon_q]. \quad (28)$$

Integrating over the spin variables we get

$$\widehat{V}|q\rangle = \varepsilon_q|q\rangle, \quad (29)$$

$$\widehat{V} = \widehat{h}\widehat{\rho} + \sum_{q'} [2\widehat{J}_{q'} - \widehat{K}_{q'}] \widehat{P} + \sum_{q'} \widehat{L}_{q'} \widehat{\Phi}. \quad (30)$$

To solve equation (29), we propose to follow the procedure introduced by Roothaan [11] and Hall [1], in which Molecular Orbitals are taken as a Linear Combination of fixed Atomic Orbitals (MO-LCAO),

$$|q\rangle = \sum_{\nu} C_{\nu q}|\nu\rangle. \quad (31)$$

Then, the matrix notation, equation (29) becomes

$$\mathbf{VC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad (32)$$

in which \mathbf{S} is the overlap matrix $\langle\mu|\nu\rangle$, \mathbf{C} is the coefficient matrix $\{C_{\nu q}\}$ which determines now the molecular orbitals as its columns, $\boldsymbol{\varepsilon}$ is a diagonal matrix composed of the orbital energies ε_q , and \mathbf{V} is the generalized Fock matrix $\langle\mu|\widehat{V}|\nu\rangle$.

Taking into account the nonorthogonality of the atomic basis set, that is,

$$\widehat{I} = \sum_q |q\rangle\langle q| = \sum_{\mu,\nu} |\nu\rangle S_{\nu\mu}^{-1} \langle\mu|, \quad \mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{I}, \quad \mathbf{S}^{-1} = \mathbf{C} \mathbf{C}^\dagger, \quad (33)$$

the following expression for matrix \mathbf{V} can be readily obtained:

$$\mathbf{V} = \mathbf{h} \mathbf{S}^{-1} \overline{\mathbf{D}} + (\mathbf{2J} - \mathbf{K}) \mathbf{S}^{-1} \overline{\mathbf{P}} + \mathbf{L} \mathbf{S}^{-1} \overline{\mathbf{\Phi}}, \quad (34)$$

where

$$h_{\mu\nu} = \langle\mu|\widehat{h}|\nu\rangle, \quad (35)$$

$$J_{\mu\nu} = \sum_{\delta,\eta,\xi,\varkappa} \langle\mu\delta|r_{12}^{-1}|\nu\eta\rangle S_{\eta\xi}^{-1} \overline{P}_{\xi\varkappa} S_{\varkappa\delta}^{-1}, \quad (36)$$

$$K_{\mu\nu} = \sum_{\delta,\eta,\xi,\varkappa} \langle\mu\delta|r_{12}^{-1}|\eta\nu\rangle S_{\eta\xi}^{-1} \overline{P}_{\xi\varkappa} S_{\varkappa\delta}^{-1}, \quad (37)$$

$$L_{\mu\nu} = \sum_{\delta,\eta,\xi,\varkappa} \langle\mu\nu|r_{12}^{-1}|\eta\delta\rangle S_{\eta\xi}^{-1} \overline{\Phi}_{\xi\varkappa} S_{\varkappa\delta}^{-1}, \quad (38)$$

$$\overline{D}_{\mu\nu} = \langle\mu|\widehat{\rho}|\nu\rangle, \quad \overline{P}_{\mu\nu} = \langle\mu|\widehat{P}|\nu\rangle, \quad \overline{\Phi}_{\mu\nu} = \langle\mu|\widehat{\Phi}|\nu\rangle. \quad (39)$$

To handle the pseudo eigenvalue and eigenvector problem, equation (32), we suggest to transform the generalized Fock matrix into an orthonormal basis:

$$\mathbf{V}' = \mathbf{X}^\dagger \mathbf{V} \mathbf{X} = \mathbf{h}' \overline{\mathbf{D}}' + (\mathbf{2J}' - \mathbf{K}') \overline{\mathbf{P}}' + \mathbf{L}' \overline{\mathbf{\Phi}}', \quad \mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{I}. \quad (40)$$

Thus, we solve for the new coefficient matrix \mathbf{C}' ,

$$\mathbf{V}' \mathbf{C}' = \mathbf{C}' \boldsymbol{\varepsilon}, \quad (41)$$

and then back transforming to the atomic basis,

$$\mathbf{C} = \mathbf{X} \mathbf{C}'. \quad (42)$$

A large number of choices for a transformation \mathbf{X} to an orthonormal space are possible. The Löwdin transformation [4], $\mathbf{X} = \mathbf{S}^{-1/2}$, is a natural choice since the transformed basis is closest to the original basis in a least-squares sense.

Having established the existence of an effective Hamiltonian, we can apply the usual Self-Consistent-Field (SCF) computational procedure to generate the basis for

fixed occupations. Then, we must return to calculate $\{\rho_q\}$ for the established one-particle functions. This iterative procedure has to be repeated until convergence is reached for the actual density matrix, which includes both effects.

5. Conclusions

In summary, we have proposed a method for the solution of the electronic structure problem which is based on a generalization of the SCF theory within the framework of the improved BCS approach for large molecules.

The approach presented is a well-comprehensible density-matrix theory which does not require the introduction of a non-interacting kinetic energy functional as in KS approaches. We developed a more general variational method which involves an arbitrary number of orbitals and fractional occupations.

It was demonstrated that the occupations $\{\rho_q\}$ can be expressed by new elements $\{\gamma_q\}$, which guarantee always the non-idempotent condition for the correlated density matrix. The direct solution for the quantities $\{\gamma_q\}$ can be performed using an algorithm where no constraint is explicitly imposed.

The obtained generalized operator \hat{V} is an effective one-particle Hamiltonian. Its eigenvalues yield the total energy including electron correlation and its eigenvectors, the one-particle functions. The new set of equations looks exactly the same as that of an independent particle HF model theory, and the MO-LCAO procedure can be applied.

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