

Analytic gradients in the improved BCS method

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The first derivatives of the total energy with respect to nuclear displacement have been calculated in the framework of the Improved Bardeen–Cooper–Schrieffer (IBCS) method. It permits the quick determination of the stationary points.

1. Introduction

The direct computation of the first derivatives of molecular energy with respect to nuclear coordinates [20] has proven to be a powerful tool in the optimization of equilibrium geometries and transition states [11,23,24]. The original development for the Hartree–Fock wave function [8,13,25,26] has been extended to correlated wave functions of the Generalized Valence Bond (GVB) type [12], to Multiconfiguration (MCSCF) [2,7] and Configuration Interaction (CI) wave functions [3,14], and also to Möller–Plesset perturbation theory [9,27,28].

Recently, we have proposed [18,19] a new method based on the Bardeen–Cooper–Schrieffer (BCS) approach to electron correlation [1]. To overcome the fact that the BCS state is not number conserving, the expectation value of the number particle operator was forced to take the given value n of electrons in the molecule. Moreover, the expression for the total energy was improved with the inclusion of the complete first-order Reduced Density Matrix (RDM). We demonstrated that with the increase of the number of electrons, our approximation becomes an adequate treatment for the electron correlation in large molecules. To distinguish our method from other approaches to molecular electron correlation based also on the BCS state [4–6,10,15–17,22,29], henceforward we will refer to it as the Improved BCS (IBCS) method.

The aim of the current work is to provide the first derivatives of the IBCS total energy with respect to nuclear coordinates so that our formalism could be implemented for determining stationary points on multidimensional potential energy surfaces.

2. The IBCS total energy

The electronic energy for a system with an even number n of electrons is given by [19]

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

where $\langle q\sigma | \hat{h} | q\sigma \rangle$ is the matrix element ($q\sigma, q\sigma$) of the kinetic energy and nuclear attraction terms (one-electron operator \hat{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. Functions $|q\sigma\rangle$ 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). P_q and Φ_q are the variational parameters which also define the occupation density:

$$\rho_q = P_q + \frac{2\Phi_q^2}{n-1}. \quad (3)$$

These parameters are not independent, they fulfill the following relations:

$$P_q = P_q^2 + \Phi_q^2, \quad (4)$$

$$2 \sum_q P_q = n. \quad (5)$$

Integrating over the spin variables in equation (1), we get the following expression for the electronic energy:

$$E_{\text{elec}} = 2 \sum_q \langle q | \hat{h} | q \rangle \rho_q + \sum_{q,q'} (2 \langle qq' | qq' \rangle - \langle qq' | qq' \rangle) P_q P_{q'} + \sum_{q,q'} \langle qq' | qq' \rangle \Phi_q \Phi_{q'}. \quad (6)$$

Let us expand our spatial orbitals in a fixed basis set:

$$|q\rangle = \sum_{\nu} c_{\nu q} |\nu\rangle. \quad (7)$$

This is the well-known procedure of taking Molecular Orbitals as Linear Combination of Atomic Orbitals (MOLCAO) [21]. Then, equation (6) becomes

$$E_{\text{elec}} = \sum_{\eta,\nu} D_{\eta\nu} \langle \eta | \hat{h} | \nu \rangle + \frac{1}{2} \sum_{\eta,\lambda,\nu,\xi} \left[P_{\eta\nu} P_{\lambda\xi} \langle \eta\lambda | v\xi \rangle + \frac{1}{2} \Phi_{\eta\nu} \Phi_{\xi\lambda} \langle \eta\nu | \xi\lambda \rangle \right], \quad (8)$$

where we have defined the following matrices:

$$D_{\eta\nu} = 2 \sum_q c_{\eta q} c_{\nu q} \rho_q, \quad (9)$$

$$P_{\eta\nu} = 2 \sum_q c_{\eta q} c_{\nu q} P_q, \quad (10)$$

$$\Phi_{\eta\nu} = 2 \sum_q c_{\eta q} c_{\nu q} \Phi_q, \quad (11)$$

and introduced the shorthand notation

$$\langle \eta\lambda | v\xi \rangle = \langle \eta\lambda | v\xi \rangle - \frac{1}{2} \langle \eta\lambda | \xi\nu \rangle. \quad (12)$$

Matrix $D_{\eta\nu}$ is obviously the density matrix. It should be noted that spatial orbitals are supposed to be real.

Finally, the total energy of a system with n electrons and N nuclei in the IBCS approximation can be written as

$$E = E_{\text{elec}} + V_{NN} = E_{\text{elec}} + \sum_A \sum_{A>B} \frac{Z_A Z_B}{R_{AB}}, \quad (13)$$

where $R_{AB} = |\mathbf{R}_A - \mathbf{R}_B|$ is the distance between the A th and B th nuclei described both by the position vectors \mathbf{R}_A and \mathbf{R}_B , respectively.

3. The energy gradients

The total energy, equation (13), depends on the molecular orbitals coefficients $\{c_{\eta q}\}$, on the parameters $\{P_q\}$ and $\{\Phi_q\}$, and on the nuclear coordinates $\{X_A\}$. Its derivative is given by

$$\frac{\partial E}{\partial X_A} = \frac{\partial \bar{E}}{\partial X_A} + \sum_{\eta,q} \frac{\partial E}{\partial c_{\eta q}} \frac{\partial c_{\eta q}}{\partial X_A} + \sum_q \left[\frac{\partial E}{\partial P_q} \frac{\partial P_q}{\partial X_A} + \frac{\partial E}{\partial \Phi_q} \frac{\partial \Phi_q}{\partial X_A} \right], \quad (14)$$

where $\partial \bar{E} / \partial X_A$ represents the derivative of all terms with explicit dependence on the nuclear coordinate X_A , and where the chain rule terms arise from the implicit

dependence of the molecular orbital coefficients and the BCS variational parameters on geometry. Differentiating equation (13) yields

$$\begin{aligned} \frac{\partial \bar{E}}{\partial X_A} &= \sum_{\eta, \nu} D_{\eta\nu} \frac{\partial \langle \eta | \hat{h} | \nu \rangle}{\partial X_A} \\ &+ \frac{1}{2} \sum_{\eta, \lambda, \nu, \xi} \left[P_{\eta\nu} P_{\lambda\xi} \frac{\partial \langle \eta\lambda | | v\xi \rangle}{\partial X_A} + \frac{1}{2} \Phi_{\eta\nu} \Phi_{\xi\lambda} \frac{\partial \langle \eta\nu | \xi\lambda \rangle}{\partial X_A} \right] + \frac{\partial V_{NN}}{\partial X_A}, \end{aligned} \quad (15)$$

$$\begin{aligned} \frac{\partial E}{\partial c_{\eta q}} &= 4 \sum_{\nu} \left[\rho_q \langle \eta | \hat{h} | \nu \rangle + P_q \sum_{\lambda, \xi} P_{\lambda\xi} \langle \eta\lambda | | v\xi \rangle + \frac{1}{2} \Phi_q \sum_{\lambda, \xi} \langle \eta\nu | \xi\lambda \rangle \Phi_{\xi\lambda} \right] c_{\nu q} \\ &= 4 \sum_{\nu} V_q(\eta\nu) c_{\nu q}, \end{aligned} \quad (16)$$

$$\frac{\partial E}{\partial P_q} = 2 \sum_{\eta\nu} c_{\eta q} c_{\nu q} \langle \eta | \hat{h} | \nu \rangle + 2 \sum_{\eta, \lambda, \nu, \xi} c_{\eta q} c_{\nu q} P_{\lambda\xi} \langle \eta\lambda | | v\xi \rangle = 2\mathcal{E}_q, \quad (17)$$

$$\frac{\partial E}{\partial \Phi_q} = \frac{16\Phi_q}{n-1} \sum_{\eta\nu} c_{\eta q} c_{\nu q} \langle \eta | \hat{h} | \nu \rangle + \sum_{\eta, \lambda, \nu, \xi} c_{\eta q} c_{\nu q} \langle \eta\nu | \xi\lambda \rangle \Phi_{\xi\lambda} = 2C_q. \quad (18)$$

In the above equations, the notations introduced in [19] have been used. $V_q(\eta\nu)$ is the generalized Fock matrix, \mathcal{E}_q is the Hartree–Fock like energy, and C_q is the correlation function.

Let us now recall the equations obtained [19] after variation of the energy with respect to c_q , P_q and Φ_q :

$$\sum_{\nu} V_q(\eta\nu) c_{\nu q} = \varepsilon_q \sum_{\nu} S_{\eta\nu} c_{\nu q}, \quad (19)$$

$$\mathcal{E}_q = \chi + \mu_q \left(\frac{1}{2} - P_q \right), \quad (20)$$

$$C_q = -\mu_q \Phi_q, \quad (21)$$

where ε_q , μ_q and χ are the Lagrangian multipliers introduced [19] to satisfy the constrains (2), (4), and (5). $S_{\eta\nu}$ is the overlap matrix.

Combining these expressions, we get

$$\begin{aligned} \frac{\partial E}{\partial X_A} &= \sum_{\eta, \nu} D_{\eta\nu} \frac{\partial \langle \eta | \hat{h} | \nu \rangle}{\partial X_A} \\ &+ \frac{1}{2} \sum_{\eta, \lambda, \nu, \xi} \left[P_{\eta\nu} P_{\lambda\xi} \frac{\partial \langle \eta\lambda | | v\xi \rangle}{\partial X_A} + \frac{1}{2} \Phi_{\eta\nu} \Phi_{\xi\lambda} \frac{\partial \langle \eta\nu | \xi\lambda \rangle}{\partial X_A} \right] + \frac{\partial V_{NN}}{\partial X_A} \end{aligned}$$

$$\begin{aligned}
& + 4 \sum_q \varepsilon_q \sum_{\eta,\nu} \frac{\partial c_{\eta q}}{\partial X_A} S_{\eta\nu} c_{\nu q} \\
& + \sum_q \left\{ [2\chi + \mu_q(1 - 2P_q)] \frac{\partial P_q}{\partial X_A} - 2\mu_q \Phi_q \frac{\partial \Phi_q}{\partial X_A} \right\}. \quad (22)
\end{aligned}$$

To evaluate the derivative of the coefficients, let us rewrite the orthonormality condition of the molecular orbitals (2) in the new basis set:

$$\sum_{\eta,\nu} c_{\eta q} S_{\eta\nu} c_{\nu q'} = \delta_{qq'}. \quad (23)$$

Differentiating equation (23), it follows that

$$2 \sum_{\eta,\nu} \frac{\partial c_{\eta q}}{\partial X_A} S_{\eta\nu} c_{\nu q'} = - \sum_{\eta,\nu} c_{\eta q} \frac{\partial S_{\eta\nu}}{\partial X_A} c_{\nu q'}. \quad (24)$$

Differentiating, also, equations (4) and (5) we obtain

$$2P_q \frac{\partial P_q}{\partial X_A} + 2\Phi_q \frac{\partial \Phi_q}{\partial X_A} = \frac{\partial P_q}{\partial X_A}, \quad (25)$$

$$\sum_q \frac{\partial P_q}{\partial X_A} = 0. \quad (26)$$

Taking into account equations (25) and (26), the last sum in equation (22) becomes zero. Hence, the final expression of the energy gradients reduces to

$$\begin{aligned}
\frac{\partial E}{\partial X_A} = & \sum_{\eta,\nu} D_{\eta\nu} \frac{\partial \langle \eta | \hat{h} | \nu \rangle}{\partial X_A} + \frac{1}{2} \sum_{\eta,\lambda,\nu,\xi} \left[P_{\eta\nu} P_{\lambda\xi} \frac{\partial \langle \eta\lambda | | v\xi \rangle}{\partial X_A} \right. \\
& \left. + \frac{1}{2} \Phi_{\eta\nu} \Phi_{\xi\lambda} \frac{\partial \langle \eta\nu | | \xi\lambda \rangle}{\partial X_A} \right] - \sum_{\eta,\nu} Q_{\eta\nu} \frac{\partial S_{\eta\nu}}{\partial X_A} + \frac{\partial V_{NN}}{\partial X_A}, \quad (27)
\end{aligned}$$

where we have defined

$$Q_{\eta\nu} = 2 \sum_q c_{\eta q} c_{\nu q} \varepsilon_q. \quad (28)$$

The derivative of the energy can be thus calculated using the molecular orbital coefficients and the derivatives of the overlap and the one- and two-electron integrals.

4. Conclusions

The IBCS analytic gradients coincide by their appearance with those obtained in the HF approximation. Even more, they generalize them. Now the orbital energies, the orbital coefficients, and the orbital occupations contain information concerning

electron correlation. Besides, a new term arises from correlation between electrons with anti-parallel spins. However, it is not necessary to compute new derivatives since this term includes only the two-electron integral derivatives. The resemblance between the IBCS and HF gradients will make easier the implementation of IBCS gradients from the available software for HF calculations in order to determine the stationary points including correlation effects.

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