

Combined Use of the Cusp Condition and the One-Electron Density Condition in the Construction of Correlated Wave Functions of Atoms and Molecules

Takashi Itoh

Department of Physics, Faculty of Science
 Ochanomizu University, Tokyo
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It is known that the exact wave function of an atom or a molecule should have a cusp at $r_{jk}=0$. On the other hand, it is known that the one-electron density associated with the Hartree-Fock wave function is, in general, close to the true density. In the present paper, it is suggested that the above two points should be taken into account in constructing an approximate wave function of an atom or a molecule.

1. Correlation between electrons in atoms and molecules

The Hamiltonian of an atom or a molecule is written as

$$H = -\frac{1}{2} \sum_j \Delta_j - \sum_{\alpha, j} \frac{Z_\alpha}{r_{\alpha j}} + \sum_{j < k} \frac{1}{r_{jk}} \quad (1)$$

in the atomic units, where $-\frac{1}{2}\Delta_j$ is the kinetic energy operator of the electron j . $-Z_\alpha/r_{\alpha j}$ is the Coulomb interaction between the nucleus α and the electron j , and $1/r_{jk}$ is the Coulomb interaction between the electrons j and k . The nuclei are treated as fixed point charges. It is difficult to obtain the exact eigen-function of the Hamiltonian H . A rather good approximation to the eigen-function is obtained in the form of a Slater determinant

$$\Phi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\mathbf{r}_1, \sigma_1) & \cdots & \phi_n(\mathbf{r}_1, \sigma_1) \\ \cdots & \cdots & \cdots \\ \phi_1(\mathbf{r}_n, \sigma_n) & \cdots & \phi_n(\mathbf{r}_n, \sigma_n) \end{vmatrix} \quad (2)$$

or a certain linear combination of such determinants. In (2), \mathbf{r}_j and σ_j denote the spatial and spin coordinates of the electron j . The functions ϕ_k are called spin orbitals.

When the spin orbitals in the determinant or the determinants are determined so as to minimize the expectation value of the energy, the Slater determinant or a certain linear combination of Slater de-

terminants appropriate to the symmetry of the atom or the molecule under consideration is called the Hartree-Fock wave function. The Hartree-Fock wave function represents the state in which each electron moves in the average field produced by the other electrons. In order to make improvement on the Hartree-Fock wave function, one has to take account of the correlation between electrons.

There are two main methods to take account of the effect of the correlation. One method is to use a linear combination of Slater determinants. This method is called CI (configuration interaction) method. In principle, the exact eigen-function can be approximated arbitrarily close by the CI method. However, the convergence is usually not rapid. The second method to take account of the correlation is to include r_{jk} explicitly in the wave function. In this method, it is easy to ensure the correct behavior of the wave function in the neighborhood of $r_{jk}=0$. However, the explicit inclusion of r_{jk} in the wave function leads to complicated integrals in the calculation of the expectation value of the energy. Thus, in either of the two methods, the computation is rather cumbersome. Therefore, it is worthwhile to search some guiding principle in the construction of an approximate wave function of an atom or a molecule to make the amount of computation smaller. The present paper is concerned with this problem.

2. Cusp condition

The Hamiltonian (1) has a singularity at $r_{\alpha j}=0$ and at $r_{jk}=0$. These singularities arise on account of the situation that the nuclei and the electrons are treated as point charges. Actually, however, the nucleus is not a point charge, but has some spread. On the other hand, the electron is commonly recognized as a point charge in the sense that the interaction between a nucleus and an electron is expressed by $-Ze^2/r$ in the Dirac equation. However, the wave function pertinent to the use in quantum chemistry is the two-component wave function obtained from the Dirac wave function through Foldy-Wouthuysen transformation followed by the disregard of the small components. This transformation brings about various magnetic interaction terms in the Hamiltonian, and besides we have a term which corresponds to the spread of the charge of the electron. Namely, the electron charge should be treated to have a spread with the mean square radius

$$\langle r^2 \rangle = \frac{3}{4} \left(\frac{\hbar}{mc} \right)^2. \quad (3)$$

The same conclusion is arrived at by a more complete quantum electro-dynamical treatment.¹⁷ The situation that the electron charge has a spread in this sense has its origin in the fact that one can not

localize the four-component Dirac wave function to a point by superposition solely of the positive energy wave functions.

When the spread of the charges of the nuclei and the electrons is taken into account, the Hamiltonian contains no singularity, and the wave function is smooth everywhere. Actually, however, the spread of the charges of the nuclei and the electrons is quite small, and the particular size of the spread does not matter in most problems of quantum chemistry. Therefore, it is practically correct to take the limit of the infinitesimal spread. The Hamiltonian (1) represents this limit. The wave function in this limit possesses a cusp at $r_{\alpha j}=0$ and at $r_{j k}=0$. These cusps are characterized by the so-called cusp condition.

The cusp condition at $r_{\alpha j}=0$ reads

$$\lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon^2} \int \frac{\partial \Psi}{\partial n} dS = -4\pi Z_{\alpha} \Psi, \quad (4)$$

where the integral is over the surface of the sphere with a small radius ε around $r_{\alpha j}=0$, and n is the outward normal. The differentiation and the integration are to be taken with respect to the coordinate of the electron j . A simple example of the cusp of this type is seen in the s type wave function of the hydrogen atom.

The cusp condition at $r_{j k}=0$ reads

$$\lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon^2} \int \frac{\partial \Psi}{\partial n} dS = 2\pi \Psi. \quad (5)$$

Here the differentiation and the integration are to be taken with respect to the relative coordinate $\mathbf{r}=\mathbf{r}_j-\mathbf{r}_k$, keeping the coordinates of the electrons other than j and k and the center of gravity of the electrons j and k fixed.

The proof of the cusp condition is as follows. First we assume the spread of the charges of the particles, and we assume that the spread is spherically symmetrical. The electrostatic interaction between two charged particles, then, is a function only of the distance between their centers. Therefore, the potential term in the Hamiltonian has the form

$$V = \sum_{\alpha, j} V_{\alpha}(r_{\alpha j}) + \sum_{j < k} V(r_{j k}). \quad (6)$$

The Hamiltonian

$$H = -\frac{1}{2} \sum_j \Delta_j + V \quad (7)$$

has no singularity, and so the eigen-function is smooth everywhere. The eigen-function satisfies the Schrödinger equation

$$-\frac{1}{2} \sum_k \Delta_k \Psi + V \Psi = E \Psi. \quad (8)$$

Now we fix the coordinates of the electrons other than j , and integrate the two sides of (8) with respect to \mathbf{r}_j within a small sphere of radius ε around the nucleus α . By Green's theorem we obtain

$$\frac{1}{\varepsilon^2} \int \frac{\partial \Psi}{\partial n} dS = \frac{1}{\varepsilon^2} \int [2(V-E)\Psi - \sum_{k \neq j} \Delta_k \Psi] dv. \quad (9)$$

We make the spread of the charges of the particles infinitesimal, and further take the limit of $\varepsilon \rightarrow 0$. Then, in the integrand of the right hand side, only the term $2V_\alpha(r_{\alpha j})$ gives a non-vanishing contribution, provided that all the $r_{\beta k}$'s except $r_{\alpha j}$ and all the r_{jk} 's are not zero. In this way we obtain (4).

In order to derive (5), we transform \mathbf{r}_j and \mathbf{r}_k to their center of gravity

$$\mathbf{r}_g = \frac{\mathbf{r}_j + \mathbf{r}_k}{2} \quad (10)$$

and the relative coordinate

$$\mathbf{r} = \mathbf{r}_j - \mathbf{r}_k. \quad (11)$$

The kinetic energy of the electrons j and k is then expressed by

$$-\frac{1}{2} (\Delta_j + \Delta_k) = -\frac{1}{4} \Delta_g - \Delta, \quad (12)$$

where Δ and Δ_g are the Laplacian operators with respect to \mathbf{r} and \mathbf{r}_g . We fix the coordinates of the electrons other than j and k and fix \mathbf{r}_g , and integrate (8) with respect to \mathbf{r} over the region $|\mathbf{r}| < \varepsilon$. We proceed further just in the same way as before, and finally obtain (5).

A more mathematical discussion on the cusp condition is found in the paper by Kato.²⁾ Further study of the behavior of the wave function in the neighborhood of $r_{\alpha j} = 0$ or $r_{jk} = 0$ has been made by Pack and Brown.³⁾

The $r_{\alpha j}$ type cusp is familiar as already pointed out with the example of the hydrogen atom. On the other hand, the r_{jk} type cusp condition can not be satisfied by a determinantal wave function. One method to incorporate the r_{jk} type cusp is to take the wave function of the form⁴⁾

$$\Psi = C\Phi, \quad (13)$$

where Φ is a determinantal wave function, while C is the correlation factor

$$C = \prod_{j < k} f(r_{jk}). \quad (14)$$

When $f(r_{jk})$ has the form

$$f(r_{jk}) = \left(1 + \frac{1}{2} r_{jk}\right) \times (\text{smooth function}), \quad (15)$$

Ψ satisfies the cusp condition at $r_{jk} = 0$.

3. One-electron density

In this section we shall explain the situation that the Hartree-Fock wave function gives a good one-electron density.⁵⁾ For simplicity, we consider the case of a single determinant.

When a single spin orbital in the determinant is replaced by some other spin orbital, we call it a single replacement. It is well known that the matrix element of the Hamiltonian between the HF wave function and a wave function obtained from the HF wave function by a single replacement is zero, provided that the spin orbitals used are orthonormal. Therefore, such single replacement wave functions are not mixed with the HF function in the first order perturbation treatment. This situation leads to the result that the one-electron density associated with the HF wave function is close to the one-electron density associated with the exact eigen-function which is to be obtained by the complete CI calculation.

As the simplest example, we consider the ground state of the He atom. The HF wave function of He has the form

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = u(\mathbf{r}_1) u(\mathbf{r}_2), \quad (16)$$

the spin part being omitted. The one-electron density associated with this wave function is given by

$$\rho(\mathbf{r}) = 2 \int |\Phi(\mathbf{r}, \mathbf{r}')|^2 d\mathbf{v}', \quad (17)$$

where the factor 2 is the number of electrons. From (16) and (17) we have

$$\rho(\mathbf{r}) = 2 |u(\mathbf{r})|^2. \quad (18)$$

Since the single replacement functions are not expected to be strongly mixed with the HF function, we first need to consider the mixing of the double replacement function of the form $v(\mathbf{r}_1) v(\mathbf{r}_2)$. As a result we shall have a CI wave function of the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sqrt{1-\eta^2} u(\mathbf{r}_1) u(\mathbf{r}_2) + \eta v(\mathbf{r}_1) v(\mathbf{r}_2). \quad (19)$$

Assuming that $u(\mathbf{r})$ and $v(\mathbf{r})$ are orthonormal, the one-electron density associated with the wave function of (19) is given by

$$\rho(\mathbf{r}) = 2 \int |\Psi(\mathbf{r}, \mathbf{r}')|^2 d\mathbf{v}' = 2 |u(\mathbf{r})|^2 + 2\eta^2 \{ |v(\mathbf{r})|^2 - |u(\mathbf{r})|^2 \}. \quad (20)$$

By comparison of (18) and (20), we see that the change in the one-electron density is of the order of η^2 , when the change in the wave function is of the order of η .

4. Combined use of cusp condition and one-electron density condition

According to Sec. 2, the correct eigen-function satisfies the cusp condition (5). On the other hand, according to Sec. 3, the correct eigen-function has the one-electron density which is close to that of the HF wave function. It will be helpful to keep in mind these two points in constructing an approximate wave function of an atom or a molecule.

As mentioned in Sec. 1, there are two methods of incorporating the correlation effects, *i. e.*, the CI method and the method of explicit inclusion of r_{jk} in the wave function.

When we adopt the r_{jk} method, we can directly incorporate the cusp condition simply by taking $f(r_{jk})$ of the form (15), as mentioned in Sec. 2. Unless the form of $f(r_{jk})$ and the orbital part Φ in (13) are chosen adequately, however, the wave function Ψ of (13) may not give a good one-electron density. On the other hand, if the CI method is used, the one-electron density will automatically be close to that of the HF wave function, as explained in Sec. 3. However, as far as the CI expansion is limited to a finite number of terms, the cusp condition is not satisfied exactly.

Thus, the two methods are complementary. When we use the $f(r_{jk})$ method, we have to be careful to adjust the parameters in the correlation factor as well as those in the orbitals so as to give a one-electron density which is close to that of the HF wave function. If we use the CI method, we have to choose configurations so as to obtain a wave function which approximately satisfies the cusp condition. In this way, the combined use of the cusp condition and the one-electron density condition will help the construction of an approximate wave function of an atom or a molecule.

As an example of the combined use of the cusp condition and the one-electron density condition, we consider the ground state of the helium atom. A wave function of the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \exp\left(\frac{1}{2} r_{12}\right) \phi(r_1) \phi(r_2) \quad (21)$$

obviously satisfies the cusp condition at $r_{12}=0$. To determine the function $\phi(r)$, one method would be to employ the energy minimization principle. However, it would be of some value to use the one-electron density condition to determine $\phi(r)$ and to compare the result with the result of the energy minimization, because this simple example is the prototype of larger atoms and molecules and the investigation of this prototype will give some insight into the correlation problems in more complicated systems.

For actual treatment, it is necessary to formulate the one-electron density condition more precisely. For this purpose, we denote the

one-electron density associated with the wave function of (21) by $\rho(\mathbf{r})$ and that of the Hartree-Fock wave function by $\rho_0(\mathbf{r})$. The function $\phi(r)$, then, is to be determined so as to make $\rho(\mathbf{r})$ as close to $\rho_0(\mathbf{r})$ as possible. This statement, however, is qualitative rather than quantitative, because we do not have any quite definite measure for the difference between $\rho(\mathbf{r})$ and $\rho_0(\mathbf{r})$. For a quantitative treatment, we need to define a measure for this difference, though there is a certain arbitrariness in this definition. We may, for example, adopt the quantity

$$A = \int [\rho(\mathbf{r}) - \rho_0(\mathbf{r})]^2 dv \quad (22)$$

as the measure for the difference between $\rho(\mathbf{r})$ and $\rho_0(\mathbf{r})$. Then, the function $\phi(r)$ is to be determined by the condition

$$A = \text{minimum}. \quad (23)$$

Detailed results of the computation on this and further examples will be reported elsewhere.

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