

An Alternative One–electron Equation including Exchange and Correlation in an Analytical Way in Terms of Equivalent Function and Phase Norm

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The ab–initio calculation for many–electron systems sets up the extremely demanding tasks which involve the explicit expression of exchange and correlation, and the calculation for the excited state in a unified way.

The Hartree–Fock equation adopts an anti symmetric wave function as the Slater determinant so as to make it possible to take into account electronic exchange in an explicit way. In this approximation, what is missing is the electronic correlation.

The Kohn–Sham equation has the decisive advantage of being framed as an one–electron equation but has bottlenecks in addressing the problems with the exclusion of self–interaction, analytical consideration of exchange and correlation. Kohn–Sham’s theory does not describe the states of electron systems with the help of anti–symmetric wavefunctions. Therefore this equation cannot but employ the additional term relevant to both exchange and correlation more or less in a factitious way.

The purpose of our work is to deduce a one–electron equation satisfying the requirement of the ab–initio calculation including the analytical consideration of exchange and correlation by introducing the concepts of the equivalent function and phase norm. Thanks to the idea for the pseudo–potential method, we establish a mapping of the equation for many–electron systems onto an effective one electron equation.

To deduce one–electron equation, we introduced the concept of equivalent function suggestive of pseudo wavefunction. It makes us shun many hardships to be faced with when manipulating many–electron equation. The goal of obtaining an one–electron equation of the desired characteristics has been satisfactorily achieved by introducing the equivalent function and the correlation–hole function in terms of the phase norm.

The mapping by means of the equivalent function yields the following one–electron equation.

$$H_{1\psi}(r_1) + \frac{N-1}{N} \left[\sum_{j=1}^N \int \Psi_j^*(r_2) H_{12\psi_j}(r_2) d\tau_2 \right] \psi(r_1) + \frac{1}{N} \left[\sum_{i=1}^N - \sum_{j \neq i} \left[\delta(m_{si}, m_{sj}) \int \psi_j^*(r_2) H_{12\psi_i}(r_2) d\tau_2 \right] \right] \psi(r_1) = \varepsilon \psi(r_1)$$

Obviously, the electronic correlation is attributed to the limitation on the configuration of electrons imposed by the reason that electrons are impossible to get infinitely close to one another due to quantum as well as classical cause. It is considered that from the point of view of quantum mechanics, the correlation between electrons is attributed to the uncertainty relation.

A variety of the methods for taking account of the electronic correlation have been proposed but the present situation of the correlation theory seems to be not in perfect harmony with the nature of electronic correlation. Since the correlation is originally relevant to the approachable limit of particles, it is consistent to take account of it through the integral of the operator term by restricting the approach of particles in a quantum–mechanical way. This problem can be resolved by inserting a correlation–hole function in terms of the phase norm into the integral of two–body operator term in the present one–electron equation without employing any additional term relevant to correlation. The correlation–hole function gives the value 1 within the admissible range of electron approach and the value 0 out of the range. The key problem is from what principle the approachable limit of electrons should be specified.

For this purpose, we use phase space. If two electrons are involved in the same volume as h of phase space, it is proved that they are in the same quantum–mechanical state. Consequently, such an approach is prohibited by the uncertainty principle. The main point of the present method consists in multiplying the integrand of the two–body operator term by a correlation–hole function determined by evaluating the phase norm for two electrons. Inserting the correlation–hole function into the obtained one–electron equation, we recast the one–electron equation so as to include the correlation effect.

This approach can be considered as an integration of the advantages of several approaches to calculation for electronic states. Unlike Hartree–Fock equation, the obtained equation is an one–electron equation which fulfills the requirement that electronic states

of many–electron systems should be determined by a single eigenvalue equation since identical particles are not distinguished from one another. In conclusion, the derived equation fulfills all the primary requirements for ab–initio calculation concerning self–interaction, exchange–correlation and one–electron equation excluding any empirical methods.

Our work can be summarized as follows.

First, we have obtained an alternative self–consistent one–electron equation for many–particle systems which describes the exchange effect in an explicit way. The deduction of the equation begins with antisymmetric wavefunction. To derive the one–electron equation, we introduced the so–called equivalent function. The equivalent function bears the meaning of the pseudo wavefunction. For this reason, the pseudo–potential method can be assessed as giving the clue to deriving a one–electron equation. This equation is based on single–electron orbitals instead of the density in DFT and has the feature of the one–electron equation analogous to the Kohn–Sham equation.

Second, we have shown that it is meaningful and useful to introduce the correlation–hole function in terms of the phase norm to consider the correlation effect in an explicit way. The phase norm reflects the cause of pure quantum correlation. In consequence, this one–electron equation resolves the self–interaction, exchange and correlation, one electron equation problems in a consistent way.