SINGLE-ELECTRON SCHRÖDINGER EQUATION FOR MANY-ELECTRON SYSTEMS

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We show that under certain conditions, an electron of a many-electron system can be described by the Schrödinger equation with a local Hamiltonian. The square root of the electron density plays the role of the wave function, and the interaction with other electrons is taken into account by averaging with the exact conditional probability. The equation dictates a redefinition of the ionization energy, which is tested with the examples of the hydrogen molecule and two-electron atoms.

1. Introduction

The theory of many-electron systems is one of the most complicated and currently central issues in quantum mechanics. Because it encompasses a spectrum of problems from the physics of atoms and molecules to solid state physics and the physics of disordered media, it has been attracting considerable interest from theoreticians for more than half a century. One of the main problems is that in many phenomena, only a single electron is of real interest. However, the many-electron interactions prevent describing the electron in the conventional terms of eigenfunctions, eigenvalues, ionization energy, excitation energy, and so on.

Certain efforts were directed toward constructing an analogue of the usual single-electron Schrödinger equation, where the influence of the other electrons (in what follows, we call them "the core") is considered in the Hamiltonian in some averaged way. The well-known Hartree–Fock (HF) approximation (see, e.g., [1]) is a certain milestone in this approach. In the HF equation, the eigenfunctions are the spin–orbitals determined by parameters identical to those for the noninteracting electrons. Under the assumption that the wave functions of the core remain unchanged after removing an electron, the ionization potentials prove to be eigenvalues (the Kupman theorem). The HF method provided considerable progress in understanding and quantitatively estimating many phenomena in atoms, molecules, and solids. However, it is not free of difficulties.

First, based on the initial model of the noninteracting electron wave function, the method takes only the exchange interaction into account. It does not involve the Coulomb interaction. In addition, the single-electron Hamiltonian of the HF method is nonlocal: the exchange electron density involved depends on the state of the electron itself [2]. This gives rise to some inconveniences because each electron appears to have "its own" Schrödinger equation. Finally, in the general case, the HF method is inconsistent with the fact that a single electron belonging to the \(N\)-electron system \((N \geq 2)\) is a mixed ensemble. In particular, this means that if \(\Psi(N)\) is the ground state wave function of the whole system, which satisfies the equation

\[
H(N)\Psi(N) = E_N\Psi(N),
\]

the mean of a single-electron operator \(\hat{a}(\nabla_r, \mathbf{r})\) resulting from averaging the operator \(\hat{A}(\nabla_r, \mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)\) over the configuration space of the core must be defined by the rule

\[
\langle \hat{a} \rangle = \langle \Psi(N)|\hat{A}|\Psi(N)\rangle.
\]

The Hamiltonian and the function $\Psi(N)$ of the HF method do not satisfy condition (2).

It might be that condition (2) gave a certain impetus to constructing and developing the presently popular density functional method due to Kohn–Sham (KSh) [3] (see also [4]). The starting points of the method are as follows. We consider a closed system of $N$ electrons and set

$$\Psi(N) = \Psi(r, \sigma; X_{N-1}),$$  \hspace{1cm} (3)

where

$$X_{N-1} = (x_2, \ldots, x_N).$$  \hspace{1cm} (4)

In formulas (3) and (4), $r$ and $\sigma$ are the respective coordinate and spin of the electron under consideration, and $x_j = (r_j, \sigma_j)$ are the corresponding variables of the other $N-1$ electrons. With

$$\int dX_{N-1} = \int dx_2 \cdots \int dx_N$$  \hspace{1cm} (5)

denoting the integration and summation over the spin-coordinate space of the core, we can define the density matrix by [5]

$$\gamma(r', r) = \sum_{\sigma} \int dX_{N-1} \Psi^*(r', \sigma; X_{N-1}) \Psi(r, \sigma; X_{N-1}).$$  \hspace{1cm} (6)

The diagonal element $\gamma(r', r)$ is related to the electron density $\rho(r)$ by the equality

$$\gamma(r, r) = \frac{1}{N} \rho(r).$$  \hspace{1cm} (7)

Central to the KSh method is the idea that the basic quantities characterizing the system (first of all, an energy) are determined by the external field and the universal functional of $\rho(r)$. This opens a possibility of replacing the real system of interacting electrons with an auxiliary model of independent electrons having the same density in the ground state. This provides a powerful tool for considering many problems and explains the popularity of the method.

Moreover, in the framework of the KSh method, a new approach (different from the HF method) to the problem of the single-electron equation has emerged. This relates not only to the equations describing independent electrons. The method contains indirect evidence that the Schrödinger equation for the function

$$\psi_0(r) = \gamma^{1/2}(r, r)$$  \hspace{1cm} (8)

is likely to exist. Indeed, if the properties of the system can be determined by specifying the electron density $\rho(r)$, then, according to relation (7), this is equivalent to the statement that the system is completely determined by the probability density $\gamma(r, r)$. We therefore cannot exclude the possibility of describing the system in terms of the pure state with wave function (8). Deriving the equation for this function was attempted in [6, 7]. However, as we show later, in spite of the explication in [6], the equation obtained in [6, 7] cannot be treated as the single-electron Schrödinger equation.

The intent of this paper is to further develop the approach initiated by [6, 7] and to establish the conditions under which function (8) can be considered the wave function of a pure state.

In Sec. 2, we formulate the basic initial relations. In Sec. 3, we use them to show the form of the Schrödinger equation for the wave function $\psi_0(r)$ and establish the conditions for its validity. Section 4 is devoted to comparing the obtained result with the corresponding HF and KSh equations. In Sec. 5, we use the examples of the hydrogen molecule and two-electron atoms to illustrate the results obtained.