

New Equation for calculating the states of atoms, molecules and solids

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Abstract

We have obtained an equation, which, according to the author, will make it much easier to calculate the states of atoms, molecules and solids. Our equation is a modified Schrodinger equation. Moreover, the Schrodinger equation, according to Nobel laureate Paul Dirac, contains all the chemical problems. The solution of this equation is simpler than the solution of the Schrodinger equation and the Hartree-Fock equations. If accurate calculations prove that this equation gives accurate results, this equation will be as important as the Schrodinger equation. This equation recorded by the author in 1986. Scientists cannot accurately solve the Schrodinger equation for multielectronic systems. Scientists cannot write down an exact but simpler equation similar to Schrodinger's equation. Scientists and scientific journals have been rejecting our equation for 36 years. However, no one has proved the wrongness or uselessness of this equation yet.

Keywords: Schrodinger equation, density functional theory, Thomas-Fermi method, Hartree-Fock equations

Introduction

The traditional approach is to take into account the Pauli principle in the wave function. In this article, an attempt to take into account the Pauli principle in the Schrodinger equation and not in the wave function. This makes it possible to determine the complete wave function in three-dimensional space, and not in 3^N dimensional space, where N is equal to the number of electrons in the system. This allows us to represent the full wave function not as a sum with a huge number of terms. The Schrodinger equation recorded here in a somewhat modified form, in which it has never been written. Solving the Schrodinger equation for a many-electron system is an extremely difficult task. Such complexity, according to the author, indicates an insufficient depth of understanding of the properties of the many-electron systems and indicates the need to search for equations that will make it easier to calculate the properties of many-electron systems.

The equation

Many-electron atoms and molecules have electrons with the same orbital moment, the same projection of the orbital moment, and the same projection of the spin. We will assume that N_i of electrons in an atom, molecule, or solid with the same spin projection, the same orbital moment and the same orbital moment projection can be describe by a one wave function $\varphi_i(\mathbf{r})$. The functions $\varphi_i(\mathbf{r})$ are normalized, but not orthonormal. We will assume that an electron in an atom is an electron cloud. We will assume that in any small volume of an atom dV there is a part N_i electrons with the same orbital moment, the same projection of the orbital moment and the same projection of the spin, equal to $N_i|\varphi_i(\mathbf{r})|^2 dV$. The Pauli principle will be taken into account as follows. We will assume that in any small volume of an atom, molecule or solid, each of the N_i electrons with the same orbital moment, the same projection of the orbital moment and the same spin projection occupies only $1/N_i$ part of this small volume. The Pauli principle will be fulfilled, since electrons with the same orbital moment, the same projection of the orbital moment and the same spin projection will occupy different volumes, or, in other words, they will be in different parts of space.

From Heisenberg's uncertainty principle

$$\Delta x^* \Delta p_x \geq \hbar/2$$

it follows that a decrease in the volume occupied by one electron by N_i times will lead to an increase in the kinetic energy of one electron by $N_i^{\frac{2}{3}}$ times. In $N_i^{\frac{2}{3}}$ times will increase that part of the kinetic energy which is not related to the movement of the electron, but is related only to the fact that the electron occupies a limited volume. The kinetic energy of N_i electrons will increase, in comparison with the energy of one electron, by $N_i^{\frac{5}{3}}$ times.

Let us write the equation

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = -\sum_{\alpha}^v \frac{\hbar^2}{2M_{\alpha}} \Delta_{\alpha} - \sum_i^t N_i^* \frac{\hbar^2}{2m} \Delta_i - N_i \sum_{\alpha,k}^{v,t} \frac{Z_{\alpha} e^2}{|\mathbf{R}_{\alpha} - \mathbf{r}_k|} + \sum_{f < j}^t N_f N_j \frac{e^2}{|\mathbf{r}_f - \mathbf{r}_j|} + \sum_i^t E_i + \sum_{\alpha < \beta}^v \frac{Z_{\alpha} Z_{\beta} e^2}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}$$

$N_i^* = N_i^{\frac{5}{3}}$ when multiplied by the part of the kinetic energy of electrons not associated with orbital motion.

$N_i^* = N_i$ when multiplied by the part of the kinetic energy of electrons associated with orbital motion.

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \text{Laplace operator}$$

t - is the number of groups of electrons with the same orbital moment, the same projection of the orbital moment and the same projection of the spin.

The equation describes a system consisting of ν nuclei and N electrons. E_i - is the energy of the electrostatic interaction between electrons belonging to the group of electrons i with the same orbital angular momentum, the same projection of the orbital angular momentum and the same spin projection. The energy E_i can be approximately found from the equation

$$\frac{N_i(N_i - 1)}{2} \varphi_i(\mathbf{r}) \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\varphi_i(\mathbf{r}')|^2 d\mathbf{r}' = E_i \varphi_i(\mathbf{r})$$

For a more accurate determination of this energy, we represent the wave function $\varphi_i(\mathbf{r})$ of the group of electrons in the form of a product of one-electron functions

$$\varphi_i(\mathbf{r}) = \varphi_{i1}(\mathbf{r}) \varphi_{i2}(\mathbf{r}) \dots \varphi_{ip}(\mathbf{r})$$

ip is the number of electrons described by the wave function $\varphi_i(\mathbf{r})$.

$$E_i = \sum_{x < y}^{ip} \int \left(\int \frac{e^2}{|\mathbf{r}_x - \mathbf{r}_y|} |\varphi_{iy}(\mathbf{r}_y)|^2 d\mathbf{r}_y \right) |\varphi_{ix}(\mathbf{r}_x)|^2 d\mathbf{r}_x$$

The wave functions $\varphi_i(\mathbf{r})$ of groups of electrons are represented as a product of one-electron functions only to take into account the correlation interaction. If we neglect the correlation interaction, in our equation it is possible to describe the properties of electrons only by functions $\varphi_i(\mathbf{r})$.

The total wave function Ψ is defined here in the ordinary three-dimensional space, and not in 3^N dimensional space and with a fixed arrangement of the nuclei, is equal to the simple product of the wave functions of groups of electrons

$$\Psi = \varphi_1(\mathbf{r}) \varphi_2(\mathbf{r}) \dots \varphi_t(\mathbf{r})$$

In the traditional approach, the wave function Ψ is equal to the determinant, which, for example, for 70 electrons is equal to the sum of more than 10^{100} terms composed of products of one-electron wave functions.

This equation differs from the Schrodinger equation by the presence of a multiplier N_i^* .

The coefficient N_i^* added to the equation for account the Pauli principle. In this case, it is not necessary to take into account the Pauli principle in the wave function. There is no need to impose additional restrictions on the wave function, to impose additional restrictions that the wave function be antisymmetric and represented as a determinant. The idea is to take the Pauli's principle into account in the equation, not in the wave function.

In the case of a hydrogen atom, $N_i=1$

$$N_i^{\frac{5}{3}} = 1^{\frac{5}{3}} = 1$$

and our equation turns into the Schrodinger equation.

For 2 s electrons, for example, with spin up, the coefficient $N_i^{\frac{5}{3}}$ is equal to

$$N_i^{\frac{5}{3}} = 2^{\frac{5}{3}}$$

The coefficient $N_i^{\frac{5}{3}}$ for 3 s electrons, for example, with spin up is equal to

$$N_i^{\frac{5}{3}} = 3^{\frac{5}{3}}$$

For n s electrons, for example, with spin up, the coefficient $N_i^{\frac{5}{3}}$ is equal to

$$N_i^{\frac{5}{3}} = n^{\frac{5}{3}}$$

If we use the concepts of the shell model and the main quantum number and assume, that one s electron, for example, with spin up, is in the first shell and has a main quantum number equal to 1, the "second" s electron with spin up is in the second shell and has a main quantum number equal to 2, and so on, s electron "numbered" n with spin up, is in the n shell and has a main quantum number equal to n, then n is the number of shells, containing s electrons with spin up, and the largest main quantum number of these electrons.

For p electrons with the same orbital moment projection and the same spin projection, the coefficient $N_i^{\frac{5}{3}}$ is equal to

$$N_i^{\frac{5}{3}} = (n - 1)^{\frac{5}{3}}$$

where (n-1) is the number of shells containing these p electrons, and n is the largest main quantum number of these p electrons.

This equation is simpler than the Hartree-Fock equations. In the Hartree-Fock equations, each electron has its own one-electron wave function. In our approach, electrons with the same orbital moment, the same projection of the orbital moment and the same spin projection, if we neglect the correlation interaction, can be described by a single wave function. In addition, the total wave function is defined in an ordinary 3-dimensional space and is equal to a simple product of such wave functions, and not a determinant consisting of a huge number of terms.

This approach has similarities with the Thomas-Fermi method and density functional theory. However, there are significant differences:

1. The Thomas-Fermi method and the density functional theory are not applicable for calculating the states of light atoms. Our equation can be used to calculate the states of light atoms. For the lightest atom, the hydrogen atom, this equation transforms into the Schrodinger equation. For the helium atom, our equation gives the same value of the energy of the ground state of the atom as the Hartree-Fock equations.
2. In the Thomas-Fermi method and density functional theory, the kinetic energy of electrons is proportional to the electron density $n(r)$ to the power of $5/3$, $n^{5/3}(r)$. In our equation, not all the kinetic energy of the electron, but only that part of the kinetic energy that is not related to the orbital motion, is multiplied by the coefficient $N_i^{5/3}$. And for each group of electrons there is its own coefficient N_i . In addition, multiplying by the coefficient $N_i^{5/3}$ and raising the electron density $n(r)$ to the power of $5/3$ is not the same thing. For example, the graph of the function $y=x$ is a straight line. The graph, for example, of the function $y=2^{5/3}x$ is also a straight line, but the graph of the function $y=x^{5/3}$ is not a straight line. Even in the case of a hydrogen atom in the Thomas-Fermi method and density functional theory, the kinetic energy is proportional to the electron density $n(r)$ to the power of $5/3$, $n^{5/3}(r)$. Moreover, the equations of the Thomas-Fermi method and the density functional theory in the case of a hydrogen atom do not pass into the Schrodinger equation. In our equation for the hydrogen atom, the kinetic energy of the electron is multiplied by the coefficient $N_i^{5/3}=1^{5/3}=1$ and our equation for the hydrogen atom turns into the Schrodinger equation.
3. The Thomas-Fermi method and the density functional theory cannot explain the periodicity of the properties of atoms in the periodic table. From our

equation follows the periodicity of the properties of atoms. The hydrogen atom has 1 s electron, for example, with spin up. The kinetic energy of the electron is multiplied by the coefficient $N_i^{\frac{5}{3}}=1^{\frac{5}{3}}=1$. In a lithium atom located in the 2nd period, there are 2 identical s electrons, for example, with spin up. The kinetic energy of these electrons is multiplied by $N_i^{\frac{5}{3}}=2^{\frac{5}{3}}$. Thus, our equation describes the qualitative changes that occur during the transition from a hydrogen atom to a lithium atom, that is, during the transition from an atom in the first period to an atom in the second period. And so on. In a sodium atom located in the 3rd period, there are 3 s electrons, for example, with spin up and the kinetic energy of these electrons is multiplied by a factor of $3^{\frac{5}{3}}$. In a potassium atom located in the 4th period, there are 4 s electrons, for example, with spin up and the kinetic energy of these electrons is multiplied by a factor of $4^{\frac{5}{3}}$. When the shells in the atom are completely filled, the kinetic energy of the s electrons of the atom is multiplied by a coefficient equal to the number of the period in which the atom is located in the periodic table, to the power of 5/3.

The kinetic energy, unrelated to the orbital motion, p electrons of the atom's, for completely filled shells, is multiplied by a coefficient equal to the number of the period in which the atom is located in the periodic table, minus 1, to the power of 5/3. This, among other things, shows that the kinetic energy of p electrons in the first period is multiplied by zero, that is, that there are no p electrons in the first period.

Thus, our equation takes into account the periodicity of the properties of atoms.

We have made calculations of the total energy for a large number of atoms. The difference between the energy found by us and the energy of the ground state of the atom was 15-20% for many-electron atoms. But the calculations of the total energy for each multi-electron atom were performed within 2 minutes using a calculator! The calculations were carried out from the first principles without using any semi empirical or fitting parameters. To simplify the calculations, it was assumed that all electrons are s electrons. In heavy atoms, even if theoretically possible states in which all electrons are s electrons, such states are very highly excited states. Moreover, comparisons were made with the energy of the ground state. The difference of 15-20% is the difference between the energy of a very, very highly excited state and the energy of the ground state. Moreover, to simplify

calculations, all electrons were described by a single wave function. Of course, for more accurate calculations, each group of electrons with the same orbital moment, the same projection of the orbital moment and the same spin projection must be described by its own wave function. In addition, to simplify the calculations, it was assumed that all wave functions are equal to one exponential function $\varphi(r)=e^{-\zeta*r}$. The parameter ζ was the same for all wave functions. Of course, for more accurate calculations, we need to choose own value of the parameter ζ for each wave function, and we need to use wave functions that have a more complex form. It is important that the energies we received were always located above the ground state energy. If the energies we found were less than the energy of the ground state, this would indicate that our equation is incorrect. In a multi-electron system, there is only one ground state and an infinitely large number of excited states. Therefore, a simple wave function chosen at random and the assumption that even in heavy atoms, all electrons are s electrons, if they correspond to some real state of the atom, then only to a very highly excited state, which, of course, must have a much higher energy than the energy of the ground state of the atom.

Conclusion

The solution of our equation is simpler than the solution of the Schrodinger equation, since the wave function in our approach is defined in the usual three-dimensional space, and not in the 3^N dimensional space. Moreover, the wave function should not be required to be antisymmetric and consist of a huge number of terms. These simplifications are achieved due to the fact, that the Pauli principle is taken into account in the equation, due to the introduction of the multiplier N_i^* . Our equation is derived from first principles without using empirical parameters and, according to the author, is accurate. Whether this equation is really accurate can be shown by more accurate calculations. If it turns out that this equation is approximate, it can be used for approximate calculation of the states of atoms, molecules and solids. If it turns out that our equation is approximate, if necessary, it can be amended to obtain more accurate results.

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