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Ferromagnetic Effect in Helium-like Atoms

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We propose a density-functional theory of ferromagnetic effect inside the helium-like atomic systems induced by the dipole-dipole interaction of the electrons. This effect gives a negative contribution to compensate the quantum mechanical result and thus to improve the violation which comes from Pauli exclusion principle considerations on the two electrons in helium-like atoms in the ground state, i.e. from Fermi hole effects.

I. INTRODUCTION

Recently, the helium-like atoms have again received many intensive studies from various modern points of view[1-3]. One active study is still the correlation of the two electrons inside the atoms. The purpose of this report is to propose a density-functional theory to treat the correlation energy of the ground state helium atom and helium-like atoms based on our past experiences on the subject of the ferromagnetism[4] and on the recent extensions of the density-functional theory to ferromagnets[5,6] which are of current interest.

In treating the two electrons in the helium-like atoms we have usually put the Coulomb interactions into the Hamiltonian. The variation method[7] gives the so-called hydrogen-like wave function (in atomic units)

$$U_2 = \frac{(Z-\frac{5}{16})^3}{\pi}\exp[-(Z-\frac{5}{16})(r_1+r_2)]$$
$$= U_1(r_1)\,U_1(r_2) \qquad (1)$$

In principle, this result is purely of electrostatic origins and no magnetic effects are involved. As we all know, every electron carries a spin magnetic dipole moment $-\mu_B$; these magnetic moments must interact with each other. The usual dipole-dipole interaction contributes a

term[8,9]

$$H_1 = -\frac{8\pi}{3}\mu_B^2 (\vec{\sigma}_1 \cdot \vec{\sigma}_2)\delta(\vec{r}_1 - \vec{r}_2) \quad . \tag{2}$$

from the singularity of r^{-1} at $r \approx 0$. The contribution of this term for the helium ground state is approximately (in atomic units)'

$$E_{QM} = 4.8\mu_B^2 \tag{3}$$

from the quantum mechanical calculation. It is an old but unsolved problem that this value is thought to be too large[9] from Pauli exclusion principle considerations. In this report we shall attack this problem by a new approach to lower this value. Before doing so, we shall bring in the density-functional considerations. In the density-functional theory, irrespective of the kind of approximation, we always put the following symmetries into consideration: First, the two electrons are identical so that the spatial distributions of these two electrons are the same. Secondly, these two electrons carry opposite spins. Following these two symmetries, locally we can never have any spin distributions and no magnetic effects will occur. Then there is no way to write down the dipole-dipole interaction such as H, in (2) above. Mathematically the above concepts can be explained as follows. The spatial distributions of both electrons in the Helium-like atom are the same, given by

$$|\psi(\vec{r})|^2 = \frac{(Z - \frac{5}{16})^3}{\pi} \exp[-2(Z - \frac{5}{16})\, r],$$

but the spin part of the wave function is dependent on the chosen good quantum numbers. It is a total spin eigenstate if the spin part is

$$|S = 0,\ S_Z = 0\rangle = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$$

where S and S_Z are the magnitude and the z-component of the total spin respectively. On the other hand the spin part may be chosen to be the simple product of either $\alpha_1\beta_2$ or $\beta_1\alpha_2$. In the density-functional theory[6] we must choose the latter form so that the density becomes

$$n(Y) = |\psi(\vec{r})|^2(\alpha^+\alpha + \beta^+\beta)$$

$$= 2|\psi(\vec{r})|^2$$

and the spin density becomes[5,6]

$$m_o(\vec{r}) = m_z(\vec{r}) \equiv \vec{\psi}^+(\vec{r})\,\sigma_z\,\vec{\psi}(\vec{r})$$

$$= | \psi(\vec{r}) |^2 (\alpha^+\alpha - \beta^+\beta)$$

$$= 0$$

In this way, we are not able to write down H_1 is in (2) because $m_0(\vec{r}) = 0$ throughout the whole space and nothing can be identified with the dipole (or σ) in H_1. However, physically, this dipole interaction definitely contributes some energies to the atom[9]. Therefore we must search for another way to treat this interaction!

First we investigate the form of interaction H_1 above. It is of the same form as the interaction Hamiltonian of the so-called Heisenberg ferromagnets[10]. Here the coupling constant $J = (16\pi/3)\mu_B^2 \delta(\vec{r}_1 - \vec{r}_2)$. The delta function nature of H_1 is the same as that of the de Gennes interaction[4,5] where the coupling constant is put as $G = -(32\pi/3)\mu_B^2$. These interactions do give rise to ferromagnetism at sufficiently low temperatures. Analogously to the treatments of these two interactions, we assume that a small part of the electron density response n, $(\vec{r})$ represents the ferromagnetic effect inside the helium-like atoms, where we also find new non-vanishing spin density $\vec{m}(\vec{r})$. These two densities $n_1(\vec{r})$ and $\vec{m}(\vec{r})$ will be the independent variables in our theory in Sec. II. In Sec. II we also calculate the contribution of this ferromagnetic effect. In Sec. III the comparison of E_{QM} and the ferromagnetic modifcations AE, are given.

II. THEORY AND CALCULATIONS

In the system of a helium-like atom we assume that a part $n_1(\vec{r})$ of the electron density involves the magnetic interactions. In the theory of Ref. 5, we have proposed a spin density

$$\vec{m}(\vec{r}) = \psi^+(\vec{r})\, a\, \psi(\vec{r}) \tag{4}$$

and the interaction energy functional of H_1 given in (2) above can be written as

$$E_1[m] = -\frac{8\pi}{3}\mu_B^2 \frac{1}{2} \int\int d\vec{r} d\vec{r}'\, \vec{m}(\vec{r}) \cdot \vec{m}(\vec{r}')\delta(\vec{r} - \vec{r}')$$

$$= -\frac{8\pi}{3}\mu_B^2 \frac{1}{2} \int d\vec{r}\, \vec{m}^2(\vec{r}) \tag{5}$$

When this part of the electron density interacts with the external electrical potential $v(\vec{r})$ and the uniform magnetic field B, the total energy functional, according to the theory of Ref. 5. can be written as

$$E[n_1,m] = \int v(\vec{r})n_1(\vec{r})d\vec{r} + \mu_B B \int m d\vec{r} + \frac{1}{2}\iint \frac{n_1(\vec{r})n_1(r')}{|\vec{r}-\vec{r}'|} d\vec{r}d\vec{r}' + G[n_1,m]$$

where $G[n_1,m]$ is calculated from the jellium model[6] which confirms the Thomas-Fermi model theory when the standard density-functional theory is followed. Here. the only difference from the elementary density-functional theory is that, the Fermi wave vectors in separated spin cases are

$$k_F^{\pm} = (6\pi^2 n^{\pm})^{1/3}$$

instead of

$$k_F = (3\pi^2 n)^{1/3}$$

in the usual case. Consequently the functional $G[n_1,m]$ is calculated as

$$G[n_1,m] = \frac{3}{20}(3\pi^2)^{2/3}\int d\vec{r}[(n_1+m)^{5/3} + (n_1-m)^{5/3}]$$

$$-\frac{3}{8}(\frac{3}{\pi})^{1/3}\int d\vec{r}\ [(n,+m)^{4/3} + (n,-m)^{4/3}] - \frac{4\pi}{3}\mu_B^2 \int d\vec{r}\, m^2 \qquad (6)$$

As mentioned in Ref. 5, here only a uniform magnetic field is exerted. Thus the only independent variable for spin density is m instead of $\vec{m}$. Further we consider that the spatial distribution of $n_1(\vec{r})$ is proportional to the total density of an electron, i.e.

$$n_1(\vec{r}) = N \sum^{occ} |\Psi(i)|^2$$

$$= N[|U_1(r)\alpha|^2 + |U_1(r)\beta|^2]$$

$$= N\frac{2}{\pi}(Z-\frac{5}{16})^3 \exp[-2(Z-\frac{5}{16})r] \qquad (7)$$

Here we define the proportionality N according to the hydrogen-like wave function given in (1) above.

Quite generally, the value of N can be varied, say, from 0 to 1. If the result of N is zero, it means that the theory predicts no magnetization or, in turn, no ferromagnetic effects. If the result of N is one, it means that the whole two electron system contributes to the ferromagnetic effect. It is reasonable to put $m(\vec{r})$ proportional to $n_1(\vec{r})$, i.e.

$$m(\vec{r}) = M\ \frac{2(Z-\frac{5}{16})^3}{\pi}\ e^{-2(Z-\frac{5}{16})r} \qquad (8)$$

where we deine the quantity M, which is also to be determined by the theory. varying from 0 to 1. Then from (6), the total energy becomes

$$E[N,M] = \int v(\vec{r})d\vec{r} + 2\mu_B BM + \frac{1}{2}\iint \frac{n_1(\vec{r})n_1(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'$$

$$+ \frac{3^{14/3}\pi^{2/3}Z^{5/3}}{2500}(Z-\frac{5}{16})^2[(N+M)^{5/3} + (N-M)^{5/3}]$$

$$-\frac{3^{13/3}Z^{4/3}}{8^3\pi^{2/3}}(Z-\frac{5}{16})[(N+M)^{4/3} + (N-M)^{4/3}]$$

$$-\frac{1}{6}\mu_B^2 Z^2 (Z-\frac{5}{16})^3 M^2 \qquad (9)$$

From the first law of thermodynamics $\delta Q = dE_{in} - Hdm$ for the uniform magnetic field H, we see that for the adiabatic process

$$\frac{\delta E[N,M]}{2\delta M} = \mu_B B$$

$$= \mu_B B + \frac{3^{11/3}\pi^{2/3}Z^{2/3}}{500}(Z-\frac{5}{16})^2[(N+M)^{2/3} - (N-M)^{2/3}]$$

$$-\frac{3^{10/3}Z^{1/3}}{128\pi^{2/3}}(Z-\frac{5}{16})[(N+M)^{1/3} - (N-M)^{1/3}]$$

$$-\frac{Z}{3}\mu_B^2(Z-\frac{5}{16})^3 M \qquad (10)$$

An alegebraic equation is thus obtained in atomic units

$$0.241 \times 2^{2/3}(Z-\frac{5}{16})[(N+M)^{2/3} - (N-M)^{2/3}] - 0.142 \times 2^{1/3}[(N+M)^{1/3}$$

$$-(N-M)^{1/3}] - 2.22 \times 10^{-6} \times 2 (Z-\frac{5}{16})^2 M = 0 \qquad (11)$$

For our ferromagnetic considerations here and in the rigorous density-functional theory which is usually a zero temperature formalism, the spin density is considered to be saturated, i.e.,

$$M = -N \qquad (12)$$

where the negative sign is due to the fact that the charge of an electron is negative in the expression of the Bohr magneton. Thus (11) reduces to

$$2.22 \times 10^{-6} \times 2^{2/3} (Z - \frac{5}{16})^2 (-M)^{2/3} - 0.382 \times 2^{1/3} (Z - \frac{5}{16})(-M)^{1/3} + 0.179 = 0 \quad (13)$$

which has the solution

$$M = -0.1/[2(Z - \frac{5}{16})^3 1 \quad (14)$$

For this saturated situation when the magnetic field is reduced to zero, the contribution of H_1 given in (2) above is obtained (in atomic units) as

$$\Delta E_Z = -\frac{1}{6} \mu_B^2 \, 2^2 (Z - \frac{5}{16})^3 M^2$$

$$= \frac{10^{-2}}{\text{---}} \text{cl;/} \; (Z - \frac{5}{16})^3 \quad (15)$$

For the ground state helium atom Z = 2 and this energy is

$$\Delta E_2 = -3 \times 10^{-4} \mu_B^2 \quad (16)$$

This value slightly reduces the value given in (3) calculated by the quantum mechanics. We shall discuss this result in the next section.

III. RESULTS AND DISCUSSION

We have proposed a ferromagnetic effect inside the helium-like atoms induced by the interaction Hamiltonian H_1 given in (2). This effect modifies the total ground state energy of these atoms. We have calculated the modifications in μ_B^2 atomic units for various helium-like systems in the Table. I. We can see that for the negative hydrogen ion the numerical modification causes the largest reduction to the value of the quantum mechanical calculation while the latter itself is the smallest in the table. That means that for this ion the violation of the Pauli exclusion is reduced most by this effect. For other systems the modifications are rather small and decrease rapidly for larger Z. It is expected that for large Z the ferromagnetic effect can be totally neglected. This could be the reason why we need not consider this ferromagnetic effect for a many-electron system.

Incidently the propositions of the spatial distributions of $n_1(\vec{r})$ and $m(\vec{r})$ in (7) and (8) respectively are different from those of the usual ferromagnetic systems. This is justified here as for atomic systems because the nuclear electric fields do hold the electrons to be distributed this way instead of the running waves of the Bloch form in solids. We do believe

that it is reasonable.

TABLE I. The values of E_{QM} and ΔE_Z in μ_B^2 atomic units.

	H^-	He	Li+	Be^{++}	$B^{(3+)}$
E_{QM}	0.325	4.80	19.4	50.1	102
ΔE_Z	-5.1×10^{-3}	-3.5×10^{-4}	-8.6×10^{-5}	-3.3×10^{-5}	-1.6×10^{-5}

Usually in the ground-state helium atoms we consider that the spins of the two electrons are strictly opposite. This can be seen from the total wave function of these atoms

$$\psi_0(\vec{r}_1, \vec{r}_2) = U_2 \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \alpha_2\beta_1)$$

where U_2 is given in (1) above. If this is unchangeable, then no other effect will occur. It is noticed that the spin part here is only its probability distributions. The dynamics in the time-dependent situations should include, say, the effect of the spin exchange between two electrons. This phenomenon could happen as has been reported theoretically in the paramagnetic vapor[2], where spontaneous spin polarizations do happen and ferromagnetism is expected. Secondly the spin polarizations in a physical system, including atomic systems, particularly in helium atoms[3] are reported to be measured accurately only up to ±5%. Any effects smaller than this value may occur. We do believe that the ferromagnetic effect mentioned in this paper may indeed occur.

(Theoretically, we may put our results in Kohn's formulation[4] to try to give here physical interpretation. Since the values of N and M given in (12) and (14) are rather small, we can write the total density as

$$n_{tot}(\vec{r}) = n_0(\vec{r}) + \delta n(\vec{r})$$

$$= (1 - N)n(\vec{r}) + Nn(\vec{r})$$

where the quantities

$$n_0(\vec{r}) \equiv (1 - N)n(\vec{r})$$

$$\delta n(\vec{r}) \equiv Nn(\vec{r}) = n_1(\vec{r})$$

Physically we interpret as: (i) $n_0(\vec{r})$ strictly obeys the Pauli exclusion principle so that the spins are half in up state and half in down state. (ii) $\delta n(\vec{r})$ is the part which avoids the Pauli exclusion principle so that it is arranged to have the spin in the direction of space quantization. Similarly for the total spin density

$$m_{tot}(\vec{r}) = m_o(\vec{r}) + m(\vec{r})$$

$$= 0 + m(\vec{r})$$

$$= Mn(\vec{r})$$

with the quantities given above.)

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