Spin polarization of light atoms in jellium: Detailed electronic structures

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We revisit the problem of the spontaneous magnetization of an *sp* impurity atom in a simple metal host. The main features of interest are as follows: (i) Formation of the spherical spin density and charge density wave around the impurity, (ii) a considerable decrease in the size of the pseudoatom in the spin-polarized state as compared with the paramagnetic one, and (iii) relevance of the electron affinity of the isolated atom to this spin polarization, which is clarified by tracing the transformation of the pseudoatom into an isolated negative ion in the low-density limit of the enveloping electron gas.

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Interests in spintronics are on the rise from both scientific and technological points of view.[1,2] Since devices in spintronics involve active control and manipulation of spin degrees of freedom in solid-state systems, it is absolutely necessary to have a deeper understanding of fundamental interactions between electron spins and its solid-state environments. In view of this situation, we are interested in a composite system of an atom immersed into the otherwise homogeneous electron gas (EG).

In an isolated atom, the ground state obeys the Hund's multiplicity rule that requires the highest spin configuration compatible with the Pauli's exclusion principle. Physically this rule is interpreted as the consequence of an effectively larger nuclear charge in a higher spin configuration due essentially to the exchange effect.[3] Similarly in a uniform EG, the same effect favors spin polarization, bringing about the spontaneous spin-symmetry breaking or the spin-density-wave state which was proven to be the ground state at arbitrary electron densities within the Hartree-Fock (exchange only) approximation.[4,5] The correlation effect, however, acts in the opposite direction[5] and this effect is so strong in an EG as to lead eventually to the paramagnetic ground state for the majority of metals.

This paper deals with the composite system of an atom immersed into the EG. Investigation of atoms embedded in the EG in both their paramagnetic[6–11] and spin-polarized[12–16] states has a long history. However, to the best of our knowledge, some important features of the electronic structure of the spontaneously spin-polarized states of this system have not been addressed so far. More specifically, they include the following: (i) the formation of the spherical combined spin density and charge density wave, which slowly decays with the distance from the impurity, (ii) significant shrinkage of spin-polarized pseudoatoms as compared with their spin-neutral counterparts, and (iii) a demonstration of how the spin-polarized states of the impurities turn into those of the negative ions of the corresponding isolated atoms as the density of the enveloping EG tends to zero. The purpose of this work is to elucidate the above points.

We are concerned with an impurity of the atomic number Z (a pseudoatom) embedded into the otherwise homogeneous EG at zero temperature characterized by its electron-density parameter $r_s=(3/4\pi n_0)^{1/3}$, where n_0 is the uniform density of the EG in the absence of the impurity. In the spin-density functional theory (SDFT),[17] the Kohn-Sham equation is written in atomic units as

$$[-(1/2)\Delta + v_\sigma^{eff}(r)]\psi_{i,\sigma}(\mathbf{r}) = \epsilon_i \psi_{i,\sigma}(\mathbf{r}), \tag{1}$$

where the spin index σ takes either $\uparrow$ or $\downarrow$, ϵ_i and $\psi_{i,\sigma}$ are, respectively, the energy level and the wave function of a Kohn-Sham electron orbital, $v_\sigma^{eff}(r)$ given by

$$v_\sigma^{eff}(r) = -Z/r + \int [n(r') - n_0]/|\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + v_\sigma^{xc}([n_\uparrow, n_\downarrow]; r) - v^{xc}(n_0) \tag{2}$$

is the effective potential, where $n(r)=n_\uparrow(r)+n_\downarrow(r)$ is the local electron density, $v_\sigma^{xc}([n_\uparrow, n_\downarrow]; r)$ defined as

$$v_\sigma^{xc}([n_\uparrow, n_\downarrow]; r) = \delta E^{xc}[n_\uparrow, n_\downarrow]/\delta n_\sigma(r) \tag{3}$$

is the spin-dependent exchange and correlation (xc) potential with $E^{xc}[n_\uparrow, n_\downarrow]$ being the total xc energy of the system, and $v^{xc}(n_0)$ is the spin-independent xc potential at the uniform electron density n_0. The spin densities are self-consistently determined as

$$n_\sigma(r) = \sum_i |\psi_{i,\sigma}(\mathbf{r})|^2. \tag{4}$$

The energy of a pseudoatom is the difference between the energies of the EG with and without the impurity,

$$E = \sum_{i \in bs} \epsilon_i + (1/2\pi) \sum_{l,\sigma} (2l+1) \int_0^{k_f} k^2 \delta'_{l,\sigma}(k) dk + \int \left\{ Z[n_0 - n(r)]/r - \sum_\sigma v_\sigma^{eff}(r) n_\sigma(r) \right\} d\mathbf{r} + (1/2) \int [n(r) - n_0][n(r') - n_0]/|\mathbf{r} - \mathbf{r}'| d\mathbf{r} d\mathbf{r}' + \int \{n(r)\epsilon^{xc}([n_\uparrow, n_\downarrow]; r) - n_0 \epsilon^{xc}(n_0)\} d\mathbf{r}, \tag{5}$$

where $\delta'_{l,\sigma}(k)$ stands for the derivative of the phase shift of the angular momentum l of the wave function for a state in

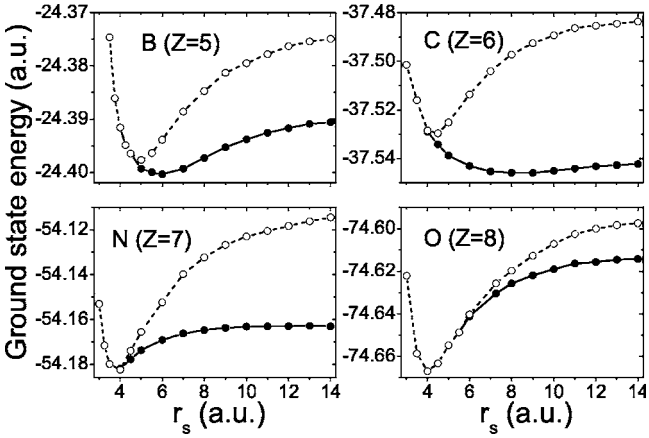

FIG. 1. Total energy of the spin-polarized (solid curves) and spin-neutral (dashed curves) states of the B, C, N, and O pseudoatoms versus the EG density parameter r_s.

the continuous spectrum in the potential in Eq. (2). In Eq. (5) the first term represents the contribution from the bound states, the second term comes from the change in the density of continuum states due to the interaction with the impurity, while all the rest are ordinary (S)DFT contributions to the total energy[18] regrouped to ensure the convergence of integrals.

We have solved Eqs. (1)–(4) self-consistently for the atoms in the first two rows of the Periodic Table immersed into the EG of various densities. For H, He, Li, Be, F, and Ne pseudoatoms, spin-neutral ground states have been found in the EG density range of $3 \leqslant r_s \leqslant 14$. For B, C, N, and O pseudoatoms, on the other hand, we found spin-polarized ground states at the density of the EG lower than certain threshold values, while the ground state was spin-neutral at higher EG densities. These conclusions agree with those of earlier studies.[15]

In Fig. 1 we plot the total energy of Eq. (5) of the spin-polarized and spin-neutral lowest-energy states of the B, C, N, and O pseudoatoms within the local spin-density approximation (LSDA) to the SDFT using the parametrization of the correlation energy of Perdew and Zunger (PZ).[19] In all the four cases, below a definite threshold value of the EG density, which is different for different impurity atoms, the spin-polarized ground state has persistently lower total energy compared with its unpolarized counterpart.

Our method of breaking the spin-symmetry was to start with imposing the occupancy of the $2p$ bound state with three electrons with spin up and less than three electrons with spin down. Then we let the system relax self-consistently to its ground state. No unoccupied bound states would remain upon the achievement of self-consistency: The $2p$ bound states we had partially filled would disappear in the self-consistent potential for spin-down electrons. For spin-up electrons, depending upon the sort of impurity atom and the density of EG, this state would either remain and then be filled with three electrons, or it would disappear as well. The net spin polarization would remain finite in either case.

The results of the calculated spin densities for the carbon atom in the EG of $r_s=6$ are shown in Fig. 2, together with

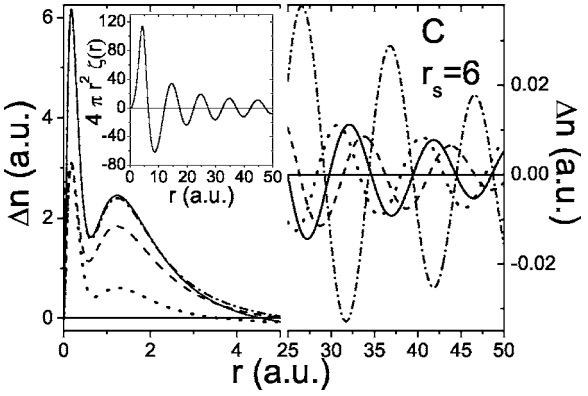

FIG. 2. Deviation of the density of electrons with spin up, spin down, and the total electron density from $n_0/2$, $n_0/2$, and n_0 (dashed, dotted, and solid curves), respectively, around the C atom in EG of $r_s=6$. The dashed-dotted curve represents the unpolarized calculation. The inset shows the local polarization of Eq. (6). All curves are multiplied by $4\pi r^2$.

the total electron density of the polarized as well as the unpolarized system. We note that at larger distances from the center, the amplitude of the Friedel oscillations of the total density in the spin-polarized state is significantly smaller than that in the neutral state, resulting in the effectively more compact pseudoatom. The latter finding is consistent with results for isolated atoms.[20] The inset in Fig. 2 shows the local polarization.

$$\zeta(r) = [n_\uparrow(r) - n_\downarrow(r)]/[n_\uparrow(r) + n_\downarrow(r)]. \tag{6}$$

The oscillating and slowly decaying local spin polarization around the impurity together with Friedel oscillations of the charge density represent a spherical combined charge-density and spin-density wave. We determine the total electronic spin of the pseudoatom as

$$S = (1/2) \int [n_\uparrow(r) - n_\downarrow(r)] d\mathbf{r}. \tag{7}$$

In Fig. 3 (left panel), the total spin of Eq. (7) is plotted against the electron-density parameter r_s. We conclude that there exists a finite net spin excess or spontaneous magnetization of the impurity in the EG at electron densities below the threshold values. The net electronic spin of Eq. (7) depends on both the atomic number of the impurity atom and the EG density, which finds itself in contrast with the result for the net charge of the impurity: Due to the full screening of a charge in the EG, which is closely related to the Friedel sum rule, the pseudoatom charge is

$$-Z = -\int [n_\uparrow(r) + n_\downarrow(r) - n_0] d\mathbf{r}, \tag{8}$$

which is uniquely determined by the sort of impurity.

While at intermediate densities of the EG the total spin of a pseudoatom is governed by complicated many-body interactions within the impurity atom-EG system, the trend in a pseudoatom's spin at low densities (large r_s) has a clear qualitative interpretation. Because of the positive electron affinity (EA) of the B, C, and O isolated atoms (0.010, 0.046,

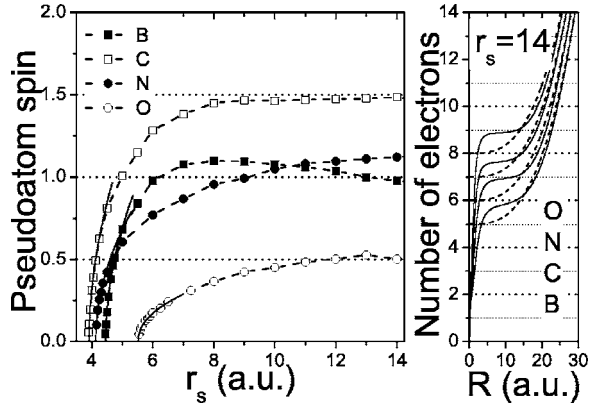

FIG. 3. Left: Spin of an impurity versus the EG density parameter r_s. Solid lines are the fittings of the data with Eq. (9). Right: The number of electrons in the sphere of radius R for pseudoatoms in EG (solid lines); $Z+(R/r_s)^3$ (dashed lines).

and 0.054 a.u., respectively,[21]) the limiting case of these atoms immersed into the EG at zero EG density are the negative ions (NI) of the corresponding atoms. According to the Hund's rule, the populations of the $2p$ orbital are with two electrons with spin up (^3P), three electrons with spin up (^4S), and three electrons with spin up, and two electrons with spin down (^2P) for B^-, C^-, and O^- ions, respectively, corresponding to the total spin of 1, 3/2, and 1/2, respectively, which is clearly satisfied in Fig. 3 at large r_s. On the other hand, the NI of the N atom is unstable although long living [EA $=-0.003$ a.u. (Ref. 21)], and the slow growth of the spin of this pseudoatom between 1 and 3/2 at large r_s can be understood as the competition between the NI ^3P and atomic ^4S states.

In the right panel in Fig. 3, the integrated number of electrons in a sphere of radius R are plotted versus the radius of the sphere for the EG of $r_s=14$. The plateaus in the case of B, C, and O close to the number of electrons of six, seven, and nine, respectively, prove unambiguously the NI character of the corresponding states, while for N this number is between seven and eight, inferring a state intermediate between an atom and NI. The growth in the number of electrons to the right from plateaus is due to the electron density approaching the constant value of n_0 at large distances from the center. This figure also shows that for a low-density EG, electrons extra to an atom or NI, whichever supported in the zero-density limit, are pushed away from the center leaving a region of nearly zero electron density between the atom or ion and the region of nearly uniform EG, where the number of electrons in the sphere of radius R is approximately $Z+(R/r_s)^3$ (dashed curves).

For the period 1 and the rest of the period 2 atoms the same arguments lead to the spin-neutrality of the corresponding pseudoatoms: In the case of H, Li, and F, which also have positive EA, the acquisition of an extra electron completes the outer shells, causing the corresponding pseudoatoms to be spin-neutral in the low-density limit. For a different reason but to the same effect, in the case of He, Be, and Ne, the spin-neutrality holds because of the nonexistence of their NI (even unstable ones with a sufficiently long lifetime[21]), while the corresponding atomic states have zero spin.

TABLE I. Best fit parameters in Eq. (9).

Atom	B	C	N	O
r_{sc}	4.46	3.91	4.13	5.52
μ	0.50	0.52	0.50	0.46
a	0.94	1.11	0.73	0.24

The steep fall in the spin of a pseudoatom near the critical point seen in Fig. 3 is suggestive of a phase transition of the second order with the power dependence of the spin on r_s near its critical value r_{sc};

$$S \approx a(r_s - r_{sc})^{\mu}. \tag{9}$$

In Table I, the best fit values of the parameters in Eq. (9) are listed. These values strongly suggest that the exponent μ is universal and equal to 0.5.[13]

At the intermediate EG densities between the threshold value and zero, the total spin of a pseudoatom obtained via Eq. (9) is not, generally speaking, a multiple of 1/2, as seen in Fig. 3. This fundamental difference between an isolated atom and the present pseudoatom is brought about by the contribution of the infinite number of delocalized electrons in the latter case.[23]

In order to make a connection to the earlier works as well as to test the sensitivity of our results to the choice of the xc potential, we have repeated the calculations for the C pseudoatom within LSDA using the parametrization of the xc energy of Gunnarsson and Lundqvist (GL)[17] and also beyond LSDA within the generalized gradient approximation (GGA) in its Perdew, Burke, and Ernzerhof (PBE) version.[22] In the former case our results for the unpolarized states reproduce those of Ref. 9. As shown in Fig. 4, regardless of the choice of the xc potential, we have been able to obtain the spin-polarized ground state of an atom embedded in the EG. While the total energies of both polarized and unpolarized

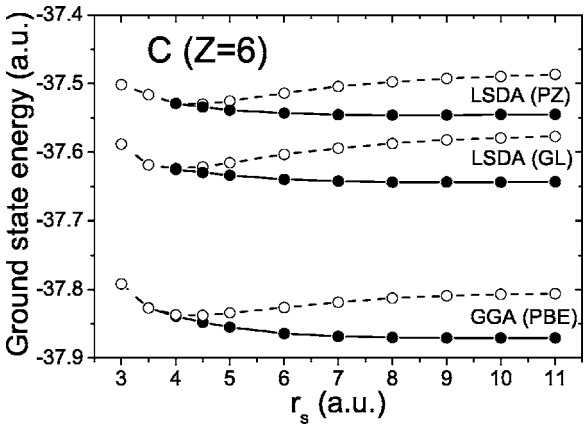

FIG. 4. Sensitivity of the energy of the C impurity to the choice of the xc potential. Solid (dashed) curves refer to the polarized (neutral) states. The xc potentials used: LSDA of Ref. 19 (PZ) and of Ref. 17 (GL), and GGA of Ref. 22 (PBE).

states are shifted depending on a specific approximation, their differences (i.e., the stabilization energy of the polarized state) does not show considerable sensitivity to the choice of the xc potential.

In conclusion, we have performed the spin-density functional calculation of the spin states of the period 1 and 2 atoms embedded in electron gas. For H, He, Li, Be, F, and Ne pseudoatoms, we have obtained the spin-neutral ground states in a wide density range of the electron gas. On the contrary, for B, C, N, and O pseudoatoms, there occurs a transition into the spin-polarized state at a critical density of the electron gas which depends on the atomic number of the impurity. Both results are in accord with earlier studies. In the spin-polarized state, the pseudoatom is found to be of a smaller effective size compared with its spin-neutral counterpart, which is a feature in common with isolated atoms. We also observe a combined spherical spin-density and charge-density wave which manifests itself as the Friedel-like oscillations. In the limit of the low density of the electron gas the electronic structure of a pseudoatom is found to converge to that of the negative ion of the corresponding isolated atom. The electronic structure of the spin-polarized state is largely different from that of the spin-neutral one, which will certainly have impact on such applications as the stopping power of metals for ions and the residual resistivity of alloys.

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