Effects of electron correlation and geometrical structure on stability of metal clusters

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A self-consistent calculation of the electronic structures of alkali-metal clusters based on the spherical jellium model has been performed by using the spin-polarized local-density-functional (LDF) approximation and its self-interaction-corrected (SIC) version. The results for the total energy of the jellium sphere lead to the stabilization of the cluster at the shell-closing numbers and the half-filled-shell ones with the high-spin configuration. The SIC calculation much improves the shortcoming of the LDF approximation and gives the correct description of the fragmentation process and the ionization potential. The effects of the nonspherical field due to certain geometrical arrangements of atoms are examined within the perturbative treatment. It is shown that the nonspherical perturbation overcomes the exchange stabilization making the half-filled-shell magic number invalid while an enhancement of the stabilization at the shell-closing numbers is still expected, particularly in the SIC version.

I. INTRODUCTION

The recent observation of the mass spectra of sodium clusters¹ has offered a very interesting concept of a "giant atom" for the metal cluster in connection with the analysis of the magic number: the pronounced abundance is observed at N = 8, 20, 40, 58, and 92 (N is the number of atoms contained in a cluster), which can be explained in analogy with the nuclear magic number by using the shell model.² That is, noninteracting atomic s electrons are bound in a spherically symmetric potential well and the enhancement of the relative stability is obtained at the shell-closing numbers of the single-electron shell. The theoretical ground of the shell model for nuclear structures may be found in the concept of the Hartree field or the mean field. All the nucleons are equally mobile because of the comparable masses of a proton and a neutron, and make a correlated motion. However, one may consider to the first approximation that they move independently in an effective field arising from the interaction between them. Then the correlated motion of nucleons causes the smoothing of this effective field and makes it rather spherical. In metal clusters we have valence electrons and core ions. Since the core ions are less mobile, they exert a static field on the valence electrons. This static field reflects the geometrical configuration of ions and is not spherical. For alkali metals, however, a large part of the static field is screened by the valence electrons and the nearly-free-electron model is a good approximation for the bulk system. Therefore one may consider, as in the case of nuclei, that the valence electrons of the clusters move independently in the smooth effective field

which loses a great part of the information on the geometrical structures of the clusters.

The calculations of the electronic structure of a jellium sphere have been done by several authors.³⁻⁷ As a matter of fact, it is possible to calculate the equilibrium geometries and other physical quantities for very small clusters (say, $N \leq 10$) without any artificial assumption.^{7,8} However, the spherical jellium model can provide us with both the qualitative and quantitative knowledge of the electronic structure over a wide range of cluster size and is suitable for understanding the essence of the physics of small clusters. Hintermann and Manninen³ have performed the spin-dependent calculation in relation to the problem of a hydrogen impurity in simple metals. Beck⁴ and Ekardt⁵ have investigated the convergence of various properties of clusters to those of the bulk. These authors, however, do not concern themselves with the problem of the magic number; that is, the preference of a specific cluster size. Chou *et al.*⁶ have calculated the second derivative (difference) of the total energy to obtain the abundance curve. We consider, however, that it is not clear that the second derivative of the total energy is proportional to the abundance curve, although it is one of the measures of the relative stability.

In the present paper we discuss the relative stability based on the energetical consideration more precisely. For this purpose we calculate the total energies of jellium spheres within the spin-polarized local-density-functional (LDF) approximation and its self-interaction-corrected (SIC) version. The spin-polarized calculation suggests the appearance of the half-filled-shell magic numbers giving a high spin configuration in addition to the shell-closing

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magic numbers. The spin-polarized calculation also enables us to evaluate the exchange energy and the stabilization by the multiplet formation. We shall show that the stabilization due to the multiplet formation is smaller than that due to the spin polarization.

By using the total energies of the ground state, we examine the possibility of the fragmentation. There the SIC results describe the fragmentation processes in a way consistent with the experimental observations. The ionization energies, which are the energies required to remove one electron from a neutral cluster, can be estimated from the orbital energies of the highest occupied orbital. The SIC calculation gives the correct gross feature of the N dependence consistent with the classical results,⁹ although a detailed feature such as the even-odd alternation observed in the photoionization experiment¹⁰ cannot be obtained within the spherical jellium model.

The spherical symmetry assumed in the present model plays an important role in determining various properties. It must be carefully examined whether or not this assumption introduces fictitious behavior. In the present paper the effect of the nonspherical field due to the geometrical configurations of atoms is examined by a perturbative treatment. This investigation supplements the detailed calculation of the electronic structure of the jellium sphere. Indeed, it will be shown that the nonspherical perturbation overcomes the exchange energy, making the stabilization at the half-filled-shell numbers ineffective although the shell-closing magic numbers are still valid.

Throughout this paper, the electron mass m, the electron charge e, and Planck's constant \hbar are taken as unity; that is, energy and length are measured in atomic units as 1 a.u.=27.21 eV and 0.529 Å, respectively. The denoting of the single-electron shell as the nl shell in this paper follows the convention in the shell model; that is, n-1 corresponds to the number of nodes of the radial wave function.

II. MODEL AND METHOD OF CALCULATION

In a spherical jellium model the positive charge is distributed uniformly in a sphere with radius R_0 determined by

$$\int d^3r \rho_+(\mathbf{r}) = N , \qquad (2.1)$$

where $\rho_+(\mathbf{r})$ is the positive charge density and N the number of atoms forming a cluster. When the positive charge density is assumed to be equal to the electron density in a bulk solid, R_0 is obtained as

$$R_0 = N^{1/3} r_{\rm s} \,, \tag{2.2}$$

where r_s is the radius of the sphere containing one electron in the bulk. Then, $\rho_+(\mathbf{r})$ is given as

$$o_{+}(\mathbf{r}) = [(4\pi/3)r_{s}^{3}]^{-1}\Theta(R_{0}-r) , \qquad (2.3)$$

with the unit step function $\Theta(x)$ and $r = |\mathbf{r}|$. The electrostatic potential due to the positive charge is not constant, contrary to the case of a bulk jellium, because of a sudden cutoff of the positive charge density at R_0 ; that is, the surface effect. Indeed, the electrostatic potential due to the positive charge is calculated as

$$v_{+}(\mathbf{r}) = \begin{cases} -(N/2R_{0})[3-(r/R_{0})^{2}], & r < R_{0} \\ -N/r, & r > R_{0} \end{cases}$$
(2.4)

The electronic structure is calculated by using the spinpolarized LDF approximation^{11,12} for the exchangecorrelation term and its SIC version.¹³ The total energy of an interacting *N*-electron system with the spin polarization $M = N_{\uparrow} - N_{\downarrow}$ (N_{σ} is the total number of electrons of spin σ) is given by

$$E_{\text{total}}(N,M) = \sum_{\alpha,\sigma} f_{\alpha\sigma} \langle \psi_{\alpha\sigma} | [-\frac{1}{2}\nabla^2 + v_+(\mathbf{r})] | \psi_{\alpha\sigma} \rangle + U[\rho_-] + E_{\text{xc}}[\rho_1,\rho_1] + U[\rho_+] , \qquad (2.5)$$

where we include the Madelung energy term $U[\rho_+]$. Here, α and σ denote the orbital state and the spin state, respectively. The electron density is related to the wave function $\psi_{\alpha\sigma}(\mathbf{r})$ as

$$\rho_{-}(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \rho_{\sigma}(\mathbf{r}) , \qquad (2.6a)$$

$$\rho_{\sigma}(\mathbf{r}) = \sum_{\alpha} \rho_{\alpha\sigma}(\mathbf{r}) = \sum_{\alpha} f_{\alpha\sigma} |\psi_{\alpha\sigma}(\mathbf{r})|^2 , \qquad (2.6b)$$

where $\sum_{\alpha} f_{\alpha\sigma} = N_{\sigma}$ and $0 \le f_{\alpha\sigma} \le 1$. The electrostatic interaction part $U[\rho_{-}]$ is explicitly given by

$$U[\rho_{-}] = \frac{1}{2} \int d^{3}r \int d^{3}r' \frac{\rho_{-}(\mathbf{r})\rho_{-}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} . \qquad (2.7)$$

The exchange-correlation part, $E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]$, is given in the local-density-functional formalism as

$$E_{\rm xc}^{\rm LDF}[\rho_{\uparrow},\rho_{\downarrow}] = \int d^3r \rho_{-}(\mathbf{r})\epsilon_{\rm xc}(\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r})) , \qquad (2.8)$$

where $\epsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow})$ is the exchange-correlation energy per electron for the homogeneous system. The present calculation is performed using the parametrized expression¹³ for $\epsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow})$ of the result of Ceperley and Alder.¹⁴ Solving self-consistently the Kohn-Sham equation,¹²

$$\left[-\frac{1}{2}\nabla^{2}+v_{\rm eff}(\mathbf{r};\alpha\sigma)\right]\psi_{\alpha\sigma}(\mathbf{r})=\epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\mathbf{r}),\qquad(2.9)$$

the total energy is obtained as

$$E_{\text{total}}^{\text{LDF}}(N,M) = \sum_{\alpha,\sigma} f_{\alpha\sigma} \epsilon_{\alpha\sigma} + U[\rho_+] - U[\rho_-] + \sum_{\sigma} \int d^3 r[\epsilon_{\text{xc}}(\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r})) - \mu_{\text{xc}}^{\sigma}(\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r}))]\rho_{\sigma}(\mathbf{r}) .$$
(2.10)

Here the effective potential $v_{\rm eff}(\mathbf{r};\alpha\sigma)$ is given by

$$v_{\rm eff}(\mathbf{r};\alpha\sigma) = v_{+}(\mathbf{r}) + \int d^{3}\mathbf{r}' \frac{\rho_{-}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu_{\rm xc}^{\sigma}(\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r})) , \qquad (2.11)$$

$$\mu_{\rm xc}^{\sigma}(\rho_{\uparrow},\rho_{\downarrow}) = \frac{\partial}{\partial\rho_{\sigma}} [\rho_{-}\epsilon_{\rm xc}(\rho_{\uparrow},\rho_{\downarrow})] .$$
(2.12)

On the other hand, within the self-interaction-corrected version,¹³ the self-interaction contribution is subtracted from the exchange-correlation energy $E_{xc}^{\text{LDF}}[\rho_{\uparrow}, \rho_{\downarrow}]$ as

$$E_{\rm xc}^{\rm SIC}[\rho_{\uparrow},\rho_{\downarrow}] = E_{\rm xc}^{\rm LDF}[\rho_{\uparrow},\rho_{\downarrow}] - \sum_{\alpha,\sigma} \left(U[\rho_{\alpha\sigma}] + E_{\rm xc}^{\rm LDF}[\rho_{\alpha\sigma},0] \right) \,. \tag{2.13}$$

Correspondingly, the effective potential in Kohn-Sham equation (2.9) is modified as

$$v_{\text{eff}}(\mathbf{r};\alpha\sigma) = v_{+}(\mathbf{r}) + \int d^{3}r' \frac{\rho_{-}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu_{\text{xc}}^{\sigma}(\rho_{\dagger}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r})) - \int d^{3}r' \frac{\rho_{\alpha\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \mu_{\text{xc}}^{\dagger}(\rho_{\alpha\sigma}(\mathbf{r}),0) .$$
(2.14)

The total energy within the self-interaction correction is obtained as

$$E_{\text{total}}^{\text{SIC}}(N,M) = \sum_{\alpha,\sigma} f_{\alpha\sigma} \epsilon_{\alpha\sigma} + U[\rho_{+}] - U[\rho_{-}] + \sum_{\alpha,\sigma} U[\rho_{\alpha\sigma}] + \sum_{\sigma} \int d^{3}r[\epsilon_{xc}(\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r})) - \mu_{xc}^{\sigma}(\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r}))]\rho_{\sigma}(\mathbf{r}) - \sum_{\alpha,\sigma} \int d^{3}r[\epsilon_{xc}(\rho_{\alpha\sigma}(\mathbf{r}),0) - \mu_{xc}^{\dagger}(\rho_{\alpha\sigma}(\mathbf{r}),0)]\rho_{\alpha\sigma}(\mathbf{r}) .$$

$$(2.15)$$

When the above formalism is applied to a spherically symmetric system, one requires further manipulation. In a central field the wave function is given by a product of an appropriate radial wave function and a spherical harmonics as

$$\psi_{\alpha}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \varphi) , \qquad (2.16)$$

where spin index σ is eliminated. If we consider partially filled *l* orbitals, that is, an open-shell configuration, and apply Eqs. (2.6) in a straightforward way, the resultant charge density and the effective potential $v_{\text{eff}}(\mathbf{r};\alpha\sigma)$ are not spherically symmetric. In order to be self-consistent, one should regard a squared wave function in Eq. (2.6b) as that averaged over the degenerate 2l+1 states as

$$\frac{1}{2l+1} \sum_{m=-l}^{l} |\psi_{\alpha}(\mathbf{r})|^{2} = \frac{1}{4\pi} |R_{nl}(\mathbf{r})|^{2}. \qquad (2.17)$$

This procedure corresponds to averaging over all possible multiplets for a given electron configuration. Therefore the calculated total energy is that averaged over all the possible states with a fixed electron configuration and spin polarization M.

III. RELATIVE STABILITY OF A JELLIUM SPHERE

A. Spin polarization

In the present paper we confine ourselves to the problem of sodium clusters, and so the calculation is performed for $r_s = 3.93$ a.u. We are interested in the relative stability of clusters of different size. In Fig. 1 the total energy per atom $\overline{E}_N = E_{\text{total}}(N, M_N)/N$ is shown as a function of the system size N for the ground-state configuration. The spin polarization M_N giving the ground state for each N is also shown. The relative stability shows downward cusps at N = 2, 5, 8, 13, 18, 19, and 20. Here, N = 2, 8, 18, and 20 are the shell-closing numbers of the 1s, 1p, 1d, and 2s shells, respectively, while N = 5, 13, and 19 are the numbers of the half-filled configuration of the 1p, 1d, and 2s shells, respectively. The stabilization at the shell-closing numbers has been demonstrated by the spin-unpolarized calculation.⁶ However, the stabilization at the half-filled configuration may be shown only by the spin-polarized one.⁷ The spin-polarized calculation of the spherical jellium model shows that the spinpolarization always takes its maximum value in the ground state. As mentioned at the end of Sec. II, this ground state corresponds to that averaged over all the multiplets with the highest spin to our approximation, averaged over ${}^{3}F$ and ${}^{3}P$ for d^{2} , ${}^{4}F$ and ${}^{4}P$ for d^{3} , and so on. Therefore, we may state that Hund's rule with respect to spin is always satisfied. Hund's rule is violated if the nonspherical perturbation due to the geometrical struc-



FIG. 1. Total energy per atom for a jellium sphere with $r_s = 3.93$ a.u. obtained within LDF (thin solid line) and SIC (thick solid line). The spin polarization M_N giving the ground state is also shown (thin dashed line).

tures of a cluster exceeds a certain critical value. This will be discussed in the following section.

From the total energies for the different spin-polarized states, we can estimate the interaction energy between electrons. Here we confine our discussion to the open 1*d*-shell configuration, which corresponds to the N = 9-18 cases. To be consistent with the spherically averaged version (2.17), the interaction energy between *d* electrons is assumed to be independent of the magnetic quantum number *m*. In general, the interaction energy for a parallel spin pair, E_{11} , is smaller than that for a antiparallel spin pair, E_{11} , because of the Pauli principle. The *d*-*d* interaction part of the total energy E_{int} is expressed as

$$E_{\text{int}} = \frac{E_{\uparrow\uparrow}}{2} \sum_{\sigma} n_{\sigma} (n_{\sigma} - 1) + E_{\uparrow\downarrow} n_{\uparrow} n_{\downarrow}$$
$$= \frac{E_{\uparrow\uparrow}}{2} n (n + 1) + \Delta \epsilon_{\text{exch}} n_{\uparrow} n_{\downarrow} , \qquad (3.1)$$

where n_{σ} is the number of *d* electrons of spin σ , $n = n_1 + n_1$, and

$$\Delta \epsilon_{\rm exch} = E_{\uparrow\downarrow} - E_{\uparrow\uparrow} . \tag{3.2}$$

The second term of Eq. (3.1) expresses the fact that the total energy is lowest when the spin polarization attains its maximum value. On the other hand, taking an average of the energies of all the allowed multiplets with a given spin polarization for the d^n configuration,¹⁵ one can express E_{int} for a given set of (n_1, n_1) in terms of Slater integrals $F^{\nu}(dd)$. Combining these results with E_{int} in Eq. (3.1), we obtain E_{11} and $\Delta \epsilon_{exch}$, explicitly as

$$E_{\uparrow\uparrow} = F^{0}(dd) - \frac{1}{14} [F^{2}(dd) + F^{4}(dd)] ,$$

$$\Delta \epsilon_{\text{exch}} = \frac{1}{14} [F^{2}(dd) + F^{4}(dd)] .$$
(3.3)

If we assume that the total-energy difference between the different spin-polarized states comes entirely from the d-d interaction energy, $\Delta \epsilon_{exch}$ can be evaluated from the present calculation of the total energies as shown in Table I. Within either the LDF or SIC approximations, $\Delta \epsilon_{exch}$ is estimated as

$$\Delta \epsilon_{\rm exch} = (3.5 \pm 0.5) \times 10^{-3} \text{ a.u.}$$
(3.4)

Here it should be noted that the straightforward integra-

tion by using the 1*d* wave function of the jellium sphere overestimates the values of $F^{\nu}(dd)$ because the correlation effect is not properly taken into account in the wave function obtained within the LDF approximation.

As already mentioned, the total energy of the ground state is lowered from that of the state with the maximum spin polarization due to the multiplet formation¹⁵ in the cases of d^2 , d^3 , d^7 , and d^8 ; that is, N = 10, 11, 15, and 16. The stabilization energy due to the multiplet formation for the ground state in all these cases is obtained in terms of Slater integrals as

$$\Delta \epsilon_{\text{mult}} = \frac{1}{98} [9F^2(dd) - 5F^4(dd)] . \qquad (3.5)$$

If we assume the ratio $F^2(dd)/F^4(dd)$ to be 1.4, which is obtained from the straightforward integration by using the 1*d* wave function of the jellium sphere, the multiplet stabilization energy $\Delta \epsilon_{\text{mult}}$ is estimated as

$$\Delta \epsilon_{\text{mult}} = 0.45 \Delta \epsilon_{\text{exch}}$$
$$= (1.6 \pm 0.2) \times 10^{-3} \text{ a.u.}$$
(3.6)

It seems that the multiplet stabilization causes no essential change in our discussion.

B. Fragmentation of the jellium sphere

In order to investigate the relative stability of clusters more precisely, let us consider a fragmentation process,

$$X_N \rightarrow X_{N-\nu} + X_{\nu}$$
,

where X denotes a constituent atom. We assume here that the possibility of the fragmentation is determined by comparing the total energies of X_N and $X_{N-\nu}+X_{\nu}$. Examining the possibility of the fragmentation processes with $\nu=1-10$, we find that the important processes are those with $\nu=1$, 2, and 8. In Fig. 2 we plot the change of the total energies after the fragmentation given as

$$\Delta E_{\mathbf{v}} = E_{\text{total}}(N - \mathbf{v}, M_{N-\mathbf{v}}) + E_{\text{total}}(\mathbf{v}, M_{\mathbf{v}})$$
$$-E_{\text{total}}(N, M_{N}) . \qquad (3.7)$$

The negative value of ΔE_{ν} means that the fragmentation is favored energetically.

TABLE I. $\Delta \epsilon_{\text{exch}}$ estimated from the energy separation between the total energies for the different spin-polarized states ($\times 10^{-3}$ a.u.).

N	Config.	LDF1*	LDF2 ^b	LDF3°	SIC1 ^a	SIC2 ^b	SIC3°
10	<i>d</i> ²	4.1			3.9		
11	d^3	3.9			3.7		
12	d^4	3.6	3.7	3.6	3.4	3.8	3.7
13	d 5	3.4	3.4	3.4	3.0	3.6	3.4
14	d^6	3.8	3.2	3.4	3.7	3.2	3.3
15	d^7	3.0			3.1		
16	d^8	2.9			3.5		

^aEstimated from $E_{\text{total}}(N,2) - E_{\text{total}}(N,0)$ for even N and $E_{\text{total}}(N,3) - E_{\text{total}}(N,1)$ for odd N. ^bEstimated from $E_{\text{total}}(N,4) - E_{\text{total}}(N,2)$ for even N and $E_{\text{total}}(N,5) - E_{\text{total}}(N,3)$ for odd N. ^cEstimated from $E_{\text{total}}(N,4) - E_{\text{total}}(N,0)$ for even N and $E_{\text{total}}(N,5) - E_{\text{total}}(N,1)$ for odd N.



FIG. 2. (a) Comparison of the energies $E_{\text{total}}(N, M_N)$ with $E_{\text{total}}(N - \nu, M_{N-\nu}) + E_{\text{total}}(\nu, M_{\nu})$ obtained by LDF for $\nu = 1$ (dashed line), $\nu = 2$ (solid line), and $\nu = 8$ (dashed-dotted line). The negative value means that the fragmentation is energetically favored. (b) Similar to (a), but obtained by SIC.

The LDF results in Fig. 2(a) show that the possible fragmentations are

 $X_{10} \rightarrow X_8 + X_2 ,$ $X_{11} \rightarrow X_9 + X_2 ,$ $X_{16} \rightarrow 2X_8 ,$ $X_{22} \rightarrow X_{20} + X_2 .$

Considering the experimental fact that the abundance of the N=9-11 and 21-24 clusters are relatively small, one may speculate that the fragmentations of these clusters cause a remarkable increase in the abundance of the N=8and 20 clusters. Our LDF results showing that the fragmentation is probable only for N=10, 11, 16, and 22 clusters seem to be inconsistent with the experimental observation.

On the other hand, the SIC results in Fig. 2(b) lead to a variety of possible fragmentations:

$$X_{11} \rightarrow X_9 + X_2 \rightarrow X_8 + X_2 + X_1 ,$$

$$X_{12} \rightarrow X_{10} + X_2 \rightarrow X_8 + 2X_2 ,$$

$$X_{13} \rightarrow X_8 + X_5 ,$$

$$X_{14} \rightarrow X_8 + X_6 ,$$

$$X_{15} \rightarrow X_8 + X_7 ,$$

$$X_{16} \rightarrow 2X_8 ,$$

$$X_{23} \rightarrow X_{21} + X_2 \rightarrow X_{19} + 2X_2 ,$$

$$X_{24} \rightarrow X_{22} + X_2 \rightarrow X_{20} + 2X_2 ,$$

$$X_{25} \rightarrow X_{17} + X_8 .$$

This variety of the possible processes is consistent with the experimental results showing the pronounced abundance of clusters N=8 and 20 relative to those of N=9-11 and 21-24. Our SIC results are inconsistent with a relatively large abundance of the N=12 and 14 clusters observed in the mass spectra. In the same way that the SIC calculation much improves the LDF results for the atomic structures,¹³ the present SIC calculation also describes the relative stability of clusters better than the LDF does.

C. Ionization energy

The ionization energy is usually estimated from the orbital energy of the highest occupied orbital. It is known, however, that the ionization potential calculated from the orbital energy within the LDF approximation does not agree with the experimental observation, while selfinteraction correction improves this disagreement.¹³ Figure 3 shows the ionization energies calculated within LDF and SIC together with those determined by the photoionization measurements.¹⁰ Here SIC drastically improves the LDF approximation and gives the correct gross feature of the N dependence consistent with the classical



FIG. 3. Ionization energies obtained by LDF (thin solid line) and SIC (thick solid line) together with the experimental results of photoionization measurements (Ref. 10) (open circles). The dashed curve represents the classical result (Ref. 9) $I_N = \varphi_{\infty} + 3/8R_0^{-1}$, where φ_{∞} is the work function of a bulk metal (2.7 eV for sodium) and R_0 a radius of a metal sphere [given by Eq. (2.2)].



FIG. 4. Schematic illustration of competition between the exchange splitting $\Delta \epsilon_{exch}$ and the nonspherical field splitting Δ .

result.⁹ In the experiments the even-odd alternation is observed. In the present calculation, however, the enhancement of the ionization energies is more remarkable at the shell-closing and half-filled-shell numbers. This discrepancy seems to be due to the artificial spherical symmetry assumed in the present model. In fact, the elaborate calculation⁸ optimizing the total energy to find the equilibrium geometry of clusters up to N = 8 gives better agreement with experiment.

IV. NONSPHERICAL PERTURBATION

As shown in the preceding section, the jellium sphere usually has a magnetic moment, as the ground-state configuration satisfies Hund's rule. For a real system, such as sodium clusters, this may not be the case because the nonspherical geometry of a cluster lifts the degeneracy of a single-electron state as shown in Fig. 4. In order to examine this possibility, we investigate the nonspherical perturbation due to the geometrical structures of clusters by regarding the spherical jellium as an unperturbed system. This treatment is similar to the ion lattice model of Lang and Kohn for metal surfaces.¹⁶ Here we investigate the N = 13 cluster with the fcc hcp, and icosahedral structures¹⁷⁻¹⁹ as shown in Fig. 5. This cluster has the largest spin polarization in the ground state of the jellium sphere.

For alkali metals it is well known that the pseudopotential theory accounts for the bulk properties very well.²⁰ The orbital energy of the sodium atom 3s electron is calculated as -3.1 eV (-5.1 eV) within the LDF (SIC) approximation,¹³ while a similar calculation, using the jellium potential for N = 1,

$$v_{jel}(\mathbf{r}) = \begin{cases} -(1/2r_s)[3-(r/r_s)^2], & r < r_s \\ -1/r, & r > r_s \end{cases}$$
(4.1)

with $r_s = 3.93$ a.u., gives -3.0 eV (-5.5 eV). In the present paper we construct the nonspherical potential by superimposing the jellium potential (4.1) as

$$V_{+}(\mathbf{r}) = \sum_{i} v_{jel}(\mathbf{r} - \mathbf{R}_{i}) , \qquad (4.2)$$



FIG. 5. Three types of N = 13 clusters.

where \mathbf{R}_i is the positional vector of the sodium atoms.

The jellium potential $v_{jel}(\mathbf{r})$ in Eq. (4.1) is transformed like $Y_{00}(\theta,\varphi)$ under the spatial rotation around the origin, $\mathbf{r}=0$; that is, rotationally invariant. Therefore, $v_{jel}(\mathbf{r}-\mathbf{R}_i)$ is necessarily expressed in terms of the rotationally invariant combination of the tensorial quantities generated from \mathbf{r} and \mathbf{R}_i . That is,

$$v_{jel}(\mathbf{r} - \mathbf{R}_i) = \sum_{l,m} v_l(\mathbf{r}, |\mathbf{R}_i|) Y_{lm}(\theta, \varphi) Y_{lm}^*(\theta_i, \varphi_i) , \qquad (4.3)$$

where θ_i and φ_i are the polar and azimuthal angles of the positional vector \mathbf{R}_i . Here it can be proved that the expansion coefficient $v_l(r,R)$ is independent of m with the help of the Wigner-Eckart theorem. In the N = 13 clusters considered here, 12 atoms are located in the first coordination shell of the center atom (hatched circles in Fig. 5). Therefore the nonspherical potential (4.1) can be expanded around the center of the cluster as

$$V_{+}(\mathbf{r}) = v_{jel}(\mathbf{r}) + \sum_{l,m} v_l(r,a) Q_{lm}^* Y_{lm}(\theta,\varphi) , \qquad (4.4)$$

where the first term is the contribution from the center atom and the second is that from the atoms in the first coordination shell. In the present calculation the interatomic distance *a* is chosen to be the same as that for the bulk solid; that is, a = 3.66 Å = 6.91 a.u. The information on the geometrical configuration of atoms in a cluster is included in the bond-orientational order parameter¹⁹ Q_{lm} defined by

$$Q_{lm} = \sum_{i=1}^{12} Y_{lm}(\theta_{i0}, \varphi_{i0}) , \qquad (4.5)$$

where θ_{i0} and φ_{i0} are the polar and azimuthal angles of the bond vector directing from the center atom (zeroth atom) to the *i*th coordinated atom.

For the clusters depicted in Fig. 5, the nonspherical expansion (4.4) is thus obtained as follows: For the face-centered-cubic (fcc) cluster which belongs to the O_h point group,

$$V_{+}^{\text{fcc}}(\mathbf{r}) = V_{0}(r)Y_{00}(\theta,\varphi) + V_{4}(r)\{Y_{40}(\theta,\varphi) + (\frac{5}{14})^{1/2}[Y_{44}(\theta,\varphi) + Y_{4-4}(\theta,\varphi)]\} + (\text{higher-order terms}).$$
(4.6a)

For the hexagonal-close-packed (hcp) cluster which belongs to the D_{3h} point group,

$$V_{+}^{hcp}(\mathbf{r}) = V_{0}(r)Y_{00}(\theta,\varphi) + iV_{3}(r)[Y_{33}(\theta,\varphi) + Y_{3-3}(\theta,\varphi)] + V_{4}(r)Y_{40}(\theta,\varphi) + (\text{higher-order terms}).$$
(4.6b)

For the icosahedral cluster which belongs to the I_h point group,

$$V_{+}^{\text{icos}}(\mathbf{r}) = V_{0}(r)Y_{00}(\theta,\varphi) + V_{6}(r)\{Y_{60}(\theta,\varphi) + (\frac{7}{11})^{1/2}[Y_{65}(\theta,\varphi) - Y_{6-5}(\theta,\varphi)]\} + (\text{higher-order terms}).$$
(4.6c)

TABLE II. Competition between the exchange stabilization and the nonspherical field stabilization for the N = 13 cluster.

	(n_1, n_1)					
Geometry	(5,0)	(4,1)	(3,2)			
fcc	0.0	$4\Delta\epsilon_{\rm exch} - \Delta_{\rm fcc} = -0.006$ a.u.	$6\Delta\epsilon_{\rm exch} - 2\Delta_{\rm fcc} = -0.019 \ {\rm a.u.}$			
hcp	0.0	$4\Delta\epsilon_{ m exch} - 2 \mid \Delta_{ m hcp} \mid \simeq 0.0$	$6\Delta\epsilon_{\mathrm{exch}} - 3 \Delta_{\mathrm{hcp}} = 0.001 \mathrm{a.u.}$			
icos	0.0	$4\Delta\epsilon_{\rm exch}=0.014$ a.u.	$6\Delta\epsilon_{\rm exch}=0.021$ a.u.			

In the present calculation we obtain the radial parts in the nonspherical expansions (4.6) by performing the twodimensional numerical integration

$$\int d\theta \sin\theta \int d\varphi Y_{lm}^*(\theta,\varphi) V_+(\mathbf{r})$$

for each r.

The wave function for the jellium sphere is represented in terms of the same basis function $Y_{lm}(\theta,\varphi)$ as that of the nonspherical potential [see Eqs. (2.16) and (4.4)]. By using the table¹⁵ of $c^k(l,m;l',m')$ defined by

$$c^{k}(l,m,l',m') = \left[\frac{4\pi}{2k+1}\right]^{1/2} \int d\theta \sin\theta \int d\varphi Y_{lm}^{*}(\theta,\varphi) Y_{km-m'}(\theta,\varphi) Y_{l'm'}(\theta,\varphi) ,$$

the matrix elements of the nonspherical perturbation are easily calculated. The configuration of the highest occupied orbital mainly determines the ground-state properties and the 1*d* orbital is the highest occupied one for the N=13 jellium sphere. Therefore we investigate the effect of the nonspherical perturbation on the *d* orbital. Hereafter we neglect the spherical term in (4.4), l=m=0, because it gives only the shift of the orbital energy.

We consider the fcc cluster first. The *d* electrons in the O_h symmetric field have been well investigated in ligand-field theory.²¹ The fivefold-degenerate *d* levels split into the twofold and threefold ones, with the energy separation $\Delta_{\rm fcc}$ given by

$$\Delta_{\rm fcc} = \frac{10}{7\sqrt{4\pi}} \int dr \, r^2 V_4(r) \, |\, R_{1d}(r) \,|^2 \,. \tag{4.7}$$

When these split levels are filled by five d electrons, the high-spin state costs $2\Delta_{fcc}$ as compared with the low-spin state [Fig. 6(a)]. However, the latter $[(n_{\uparrow}, n_{\downarrow})=(3,2)]$ costs the d-d interaction energy $6\Delta\epsilon_{exch}$ as compared with the former $[(n_{\uparrow}, n_{\downarrow})=(5,0)]$ [Eq. (3.1)]. The competition between the nonspherical stabilization and the stabilization due to the exchange effect determines whether or not the high-spin state is realized in the ground state. By using the 1d wave function of the N = 13 jellium sphere obtained from the spin-unpolarized LDF calculation, the nonspherical field splitting is calculated as

$$\Delta_{\rm fcc} = 2.0 \times 10^{-2} \text{ a.u.} \tag{4.8}$$

As shown in Table II, the stabilization due to the nonspherical perturbation overcomes that due to the exchange effect and prohibits the high-spin configuration in the ground state in the fcc cluster.

For the hcp cluster the situation is slightly more complicated. The perturbation $V_3(r)$ generates the mixing between the 1p and 1d orbitals. Estimating that the energy change for the $(l,m)=(2,\pm 2)$ states by considering this mixing is as small as one-tenth of the unperturbed p-d separation, we neglect the $V_3(r)$ term in the following. As shown in Fig. 6(b), the $V_4(r)$ term causes the splitting of the d level into two twofold-degenerate states and one nondegenerate state, with the separation Δ_{hcp} given by

$$\Delta_{\rm hcp} = \frac{5}{7\sqrt{4\pi}} \int dr \, r^2 V_4(r) \, |\, R_{1d}(r) \,|^2 \,. \tag{4.9}$$

The energy difference between the high-spin and low-spin state is in this case $3\Delta_{hcp}$ [Fig. 6(b)]. The separation Δ_{hcp} is calculated as

$$\Delta_{\rm hcp} = -6.8 \times 10^{-3} \text{ a.u.} \tag{4.10}$$

As shown in Table II, the nonspherical stabilization effect



FIG. 6. High- and low-spin configurations under the non-spherical fields due to (a) the fcc and (b) hcp geometry.

turns out to be important. It should be noticed here that, for the d^5 configuration, the multiplet stabilization effect for the excited spin quartet and doublet states reduces the spin-pairing energies, which are the energies required for the excitations to the lowest multiplets of these quartets and doublets. Assuming that $F^2(dd)/F^4(dd) = 1.4$, as was done before in evaluating the multiplet stabilization energy for the ground multiplet [Eq. (3.6)], we find that the spin-pairing energy is reduced by 20% from that estimated by use of $\Delta \epsilon_{\rm exch}$.

From the above estimation, we conclude that the appearance of the half-filled-shell magic numbers suggested by the jellium sphere model is suspicious for the real sodium clusters. This fact also suggests that the fine structures observed at N = 11-18 in the mass spectra of sodium clusters is caused by the nonspherical perturbation. Actually, Clemenger²² has examined the effect of the ellipsoidal deformation by using the modified Nilsson model and shown that some of the fine structures are reproducible. However, we wonder if the ellipsoidal deformation could simulate reasonably the nonspherical perturbation due to the geometrical structure of the real cluster.

For the icosahedral cluster, the expansion (4.6c) includes only higher-order terms $(l \ge 6)$ which give the vanishing matrix elements for the *d* states. Unfortunately, from the present perturbative treatment, we cannot obtain the reliable information on the relative stability of the fcc, hcp, and icosahedral geometries because of the ambiguity in the evaluation of the Madelung energy $U[\rho_+]$. However, if the nonspherical potential can be treated as a perturbation acting on the jellium sphere, there is no reason why the icosahedral cluster is stable compared with the fcc and hcp ones for the N=13 sodium cluster in the sense that it gains no structural energy (Table II).

Finally, we examine whether or not the shell-closing magic numbers are still valid even when the nonspherical perturbation is taken into account. As shown schematically in Fig. 7, the nonspherical field splitting Δ competes with the energy separation $\Delta \epsilon_{orb}$ between the highest occupied orbital and the lowest unoccupied one. In Table III the orbital energies of the highest occupied and the lowest unoccupied orbitals and their separation are shown for the shell-closing numbers. Within the LDF approximation the orbital energies for the occupied states involve the large self-interaction error and the energy separation between the highest occupied and the lowest unoccupied states is considerably underestimated. The SIC version



FIG. 7. Schematic illustration of competition of the energy separation between the highest occupied and the lowest unoccupied orbitals $\Delta \epsilon_{orb}$ with the nonspherical field splitting Δ .

numbers (a.u.).						
N		LDF	SIC			
8	ϵ_{1d}	-0.065	-0.066			
	ϵ_{1p}	-0.121	-0.165			
	$\Delta \epsilon_{ m orb}$	0.056	0.099			
18	ϵ_{2s}	-0.103	-0.102			
	ϵ_{1d}	-0.115	-0.148			
	$\Delta \epsilon_{ m orb}$	0.012	0.046			
20	ϵ_{1f}	0.081	-0.085			
	ϵ_{2s}	-0.101	-0.137			
	$\Delta\epsilon_{ m orb}$	0.020	0.052			

TABLE III. Orbital energies of the lowest unoccupied and

highest occupied states and their separation at the shell-closing

essentially improves this shortcoming of the LDF approximation.¹³ By assuming that the nonspherical field splitting Δ is approximately of the same order of magnitude as that estimated for the case of N = 13, Eqs. (4.8) and (4.10), and using the values of energy gap $\Delta \epsilon_{orb}$ obtained from the SIC calculation, we conclude that the shellclosing magic numbers are still valid even if the nonspherical perturbation is taken into account.

V. SUMMARY AND CONCLUSION

The self-consistent calculation of the electronic structures of the jellium sphere has been performed by using the spin-polarized local-density-functional approximation and its self-interaction-corrected version. The results for the total energy of the jellium sphere support the stabilization of the cluster at the shell-closing numbers. The spherical symmetry assumed in the present model leads to the additional feature of the relative stabilization at the half-filled-shell numbers with the high-spin configuration. The SIC calculation drastically improves the quantitative errors arising from the LDF approximation and gives the correct description of the fragmentation process and the ionization potential. The effect of the nonspherical field due to the geometrical configuration of atoms in the cluster is examined within the perturbative treatment. It is shown that the nonspherical perturbation overcomes the exchange stabilization, making the half-filled-shell magic number invalid while the stabilization at the shell-closing numbers is still effective. In conclusion, the SIC formalism is one of the possible ways of improving the shortcomings of the LDF approximation in the calculation of small clusters.

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