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Feasibility of cluster calculations in describing impurities in simple metals

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The spin-density-functional formalism has been applied to study electronic properties of small spherical clusters of an ideal free-electron metal (jellium). The electronic structure of a hydrogen atom embedded in the center of the cluster has been calculated as a function of the cluster size. A comparison of the results to the exact limit of the hydrogen atom in an infinite jellium shows that a large cluster size (about 100 atoms) is needed for an accurate description of the electronic structure of the impurity. Self-consistent unrestricted Hartree-Fock calculations have been performed for small Li clusters with a hydrogen impurity, and the results are compared with those of the jellium model. As an effect of the finite cluster size, both calculations show similar features in the cluster properties. Methods for calculating the impurity Knight shift using the cluster technique have been studied.

I. INTRODUCTION

In the cluster method the infinite solid is described by a finite small cluster of atoms.[1,2] This cluster can be embedded in an infinite effective medium or, as in the present study, it can be a free macromolecule in the vacuum. In the latter case the computational techniques of quantum chemistry can be applied to calculate the electronic structure of the cluster. The cluster method becomes useful when the periodicity of the lattice is broken and hence the main application in the metal physics has been adsorbates on metal surfaces[1-3] and impurities.[4] On the other hand, recent progress in experimental small-metal-cluster techniques[5] will be a test field for cluster calculations. Here, the possibility of calculating the electronic structure for metal clusters of arbitrary geometry will be of importance.

The origin of the present work were some intriguing results of self-consistent unrestricted Hartree-Fock (UHF) calculations for 6- and 22-Li atom clusters with and without a hydrogen impurity in the center.[6] There, the question of extrapolation of electronic cluster properties to bulk metal properties was raised. Since this question is common to all kinds of cluster calculations, it is very desirable to have a simple model where the cluster size can be varied up to the infinite (bulk) cluster limit.

A comparison of the results of the cluster calculation to those of an infinite system shows the cluster size needed in describing the properties of macroscopic material. In a perfect metal the comparison can be made to the results of a band-structure calculation.[7] In most applications, however, the exact result for the infinite system is not known and one has to increase the cluster size in order to find an asymptotic behavior of the calculated properties, or compare the results to experiments.

In this paper we make a model calculation for studying the applicability of the cluster method to describe the electronic structure of an (hydrogen) impurity in simple metals. We describe the metal by a jellium cluster, i.e., an interacting electron gas with a compensating homogeneous positive background charge which is enclosed in a finite sphere. In this model there is no lattice structure and one can create arbitrary size spherical clusters. A similar jellium model has been used earlier by Martins *et al.*[8] for studying the dependence of the ionization potential on the cluster size. By embedding the hydrogen nucleus in the center of the cluster the electronic structure of this impurity can be studied as a function of the cluster radius. The electronic structure of atoms embedded in an infinite jellium can be calculated exactly in the same basis[9] and compared to the results of the cluster calculations. This has been done for $r_s = 3.25$ corresponding to Li metal.

The cluster method has also been applied to study magnetism of metals.[10,6] Owing to the finite number of electrons the magnetic properties of small metallic clusters may be very different from those of the bulk metal.[11,12] The ground state of a small cluster of nonmagnetic metal is usually magnetic.[6,11] This is an interesting phenomenon as such but it causes difficulties in applying the cluster technique to describe the magnetic properties of the bulk metal. We have studied different ways of calculating Knight shift at a hydrogen atom in jellium using the cluster method. The results indicate that the main features of the contact spin density can be described already with a few tens of atoms, but the extracting of reliable quantitative results from cluster calculations is difficult.

In Sec. II we describe our model and specify the density-functional technique used for calculating the electronic structure. The results for pure jellium clusters are discussed in Sec. III, where the density of states, bandwidth, total energy, and the surface energy of the cluster are compared to those of the infinite jellium. The results for the electronic structure of the hydrogen impurity are given in Sec. IV. In Sec. V we compare the charge densities of 22-atom jellium clusters with and without a hydrogen impurity in the center to those obtained from spin-polarized Hartree-Fock calculations. Methods for estimating the spin density around the impurity are studied in Sec. VI and the conclusions are given in Sec. VII.

II. JELLIUM CLUSTER MODEL

In the jellium model a metal is described by a homogeneous electron gas with a compensating positive background charge which corresponds to the positive ions in the real metal. Surfaces,[13] vacancies, voids, and impurities[14] in simple metals have been studied extensively by starting from the jellium model. Consistently with earlier studies we define the jellium cluster as a spherical rigid positive charge distribution and a corresponding amount of interacting electrons. The positive background charge distribution is

$$n_+(\vec{r})=n_0\Theta(R-|\vec{r}|)\,, \tag{1}$$

where n_0 is the density of the jellium, usually defined with help of the electron-gas density parameter $r_s=(4\pi n_0/3)^{-1/3}$. Θ is the unit step function and R the cluster radius,

$$R=N^{1/3}r_s\,, \tag{2}$$

where N is the number of electrons in the cluster (which is assumed to be neutral). When an impurity atom is added in the center of the cluster the positive charge distribution will be

$$n_+(\vec{r})=n_0\Theta(R-r)+Z\delta(r),\quad r=|\vec{r}| \tag{3}$$

where Z is the nuclear charge of the impurity. The total number of electrons in the neutral cluster with an impurity is $N+Z$.

Owing to the spherical symmetry of $n_+(\vec{r})$ the cluster is like a large atom (with an unusual nuclear charge distribution) and the electronic structure is straightforward to compute numerically. In the

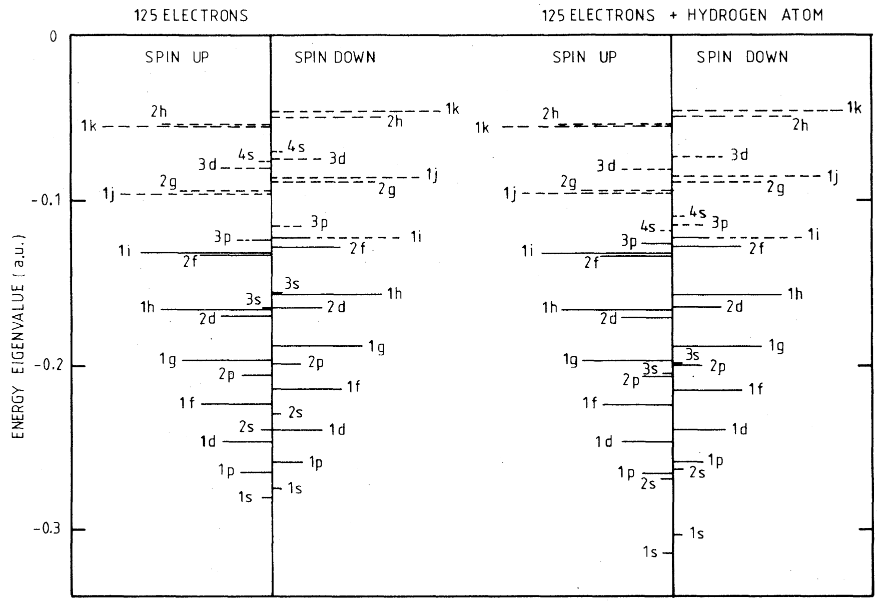

FIG. 1. One-electron eigenvalues for the 125-electron jellium cluster with and without a hydrogen impurity. The dashed lines denote empty levels above the Fermi energy. The length of each line is proportional to the degeneracy of the state.

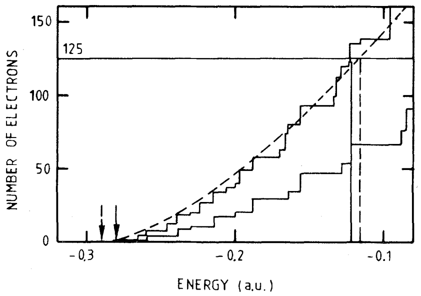

FIG. 2. Integrated density of states of the 125-electron jellium cluster compared to that of the infinite jellium (dashed line). The lower solid line gives the integrated density of states for the spin-down electrons. The Fermi surface is denoted by a vertical line and the bottom of the band with an arrow.

present work we use the density-functional formalism with the local spin-density approximation of Gunnarsson and Lundquist,[15] and compute the electronic structure fully self-consistently with a modified Herman-Skillman[16] code.

III. RESULTS FOR PURE CLUSTERS

The jellium is characterized only by the electron density parameter r_s for which we have chosen the value $r_s = 3.25$, corresponding to Li metal. The energy eigenvalues for a cluster with 125 electrons are shown in Fig. 1. For smaller clusters the occupation of the levels follows nearly the same picture. When the cluster size increases, more and more electrons are in states with a large angular momentum eigenvalue whereas only a few electrons have s character. (Throughout the paper, the s character of the one-electron-cluster wave functions is always referred to the center of the cluster.) It is interesting to notice that for each spin in the 125-electron clusters there are only three s states occupied. In the ground state the $3p$ and $1i$ states are only partially filled leading to a polarized state with a total polarization of $\zeta_0 = 0.088$, where ζ_0 is defined as $\zeta_0 = (N^\uparrow - N_\downarrow)/(N^\uparrow + N^\downarrow)$, $N^\uparrow$ and $N^\downarrow$ being the numbers of spin-up and spin-down electrons in the cluster, respectively. For smaller clusters the population of the levels follows Hund's rules leading practically always to a polarized ground state.

The integrated density of states of the 125-electron cluster is shown in Fig. 2 and compared to the result of an infinite jellium. The overall agreement between the two results is good but the density of states of the cluster calculation has still fairly much structure. One pecularity is the wide plateau below the Fermi level. This corresponds to a large gap in the density of state and averaging the δ-function states by Gaussians would lead to a minimum in the density of states. This kind of minimum is also seen by Salahub and Messmer[7] in their molecular-orbital cluster calculations for the same size of Al cluster (129 electrons). In the light of the present calculation the existence of the minimum may be an artifact of the cluster size: Decrease of the cluster size would move the minimum towards the Fermi energy and finally above the Fermi energy. Thus the comparison of the detailed structure of the density of states of the cluster calculations to the experimental results has to be taken with caution.

The bandwidth can be defined as the difference of the highest and the lowest occupied states. Figure 3 shows the calculated bandwidth as a function of the cluster radius. The bandwidth approaches to the asymptotic value slowly and fluctuates strongly depending on the configuration of the cluster. This is due to the large degeneracy of the single-particle states: The bandwidth has a minimum when the highest occupied state is full. For comparison to the

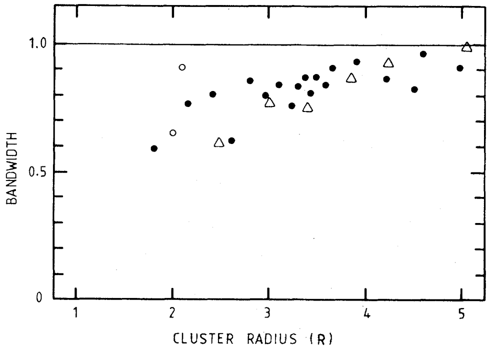

FIG. 3. Bandwidth as a function of the cluster radius. The black dots are results for the jellium clusters, the triangles for $X\alpha$ calculations of Ref. 7, and the open circles for Hartree-Fock calculations of Ref. 17. The cluster bandwidth is given in the units of the bandwidth of the infinite system.

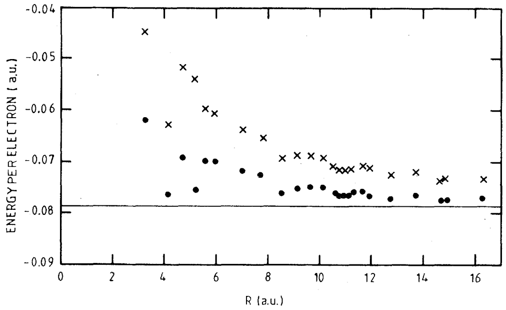

FIG. 4. Total energy per electron in the cluster as a function of the cluster radius (crosses). The dots are the results after subtracting the surface energy.

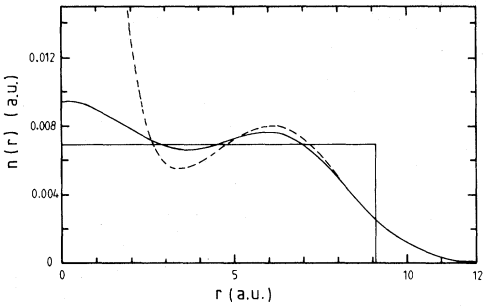

FIG. 5. Electron density in a 22-electron cluster with (dashed line) and without (solid line) the hydrogen impurity. The homogeneous positive background charge is also shown.

jellium results Fig. 3 also shows some results for molecular-orbital $X\alpha$ calculations of Al clusters[7] and Hartree-Fock calculations of Li clusters.[17] It is interesting to see that in these metals the jellium clusters give very well the general trend of the increase of the density of states with the cluster size.

The asymptotic limit for the total energy of the cluster is $N\epsilon$, where ϵ is the energy per electron in an infinite electron gas. For small clusters the surface energy is a large contribution to the total energy. For large clusters the surface energy approaches that of a flat jellium surface,[13,18] and ϵ can be estimated as

$$\epsilon = E_{\text{tot}}/N - 4\pi R^2 \delta / N \, , \tag{4}$$

where E_{tot} is the total energy of the cluster, and δ the surface energy for a flat jellium surface. The calculated ϵ as a function of the cluster radius is shown in Fig. 4, where also the results without substracting the surface term are plotted. Both results approach the asymptotic limit of an infinite jellium very slowly. The surface energies of the sphere are larger than that of a flat surface ($\delta = 200$ erg/cm^2 for $r_s = 3.25$) and thus even after substracting the surface energy ϵ stays above the asymptotic limit.

IV. HYDROGEN IMPURITY IN THE CLUSTER

In order to test the applicability of the cluster approach to the impurity problem we calculated the electronic structure of a hydrogen in the center of the jellium cluster ($r_s = 3.25$). The electron-density profiles in a cluster of 22 electrons with and without the hydrogen atom are shown in Fig. 5. In small clusters the electron density of the pure cluster is fairly inhomogeneous and in studying the effect of the hydrogen atom one can define the density difference,

$$\delta n(r) = n_{\text{H}}(r) - n(r) \, , \tag{5}$$

where $n_{\text{H}}(r)$ and $n(r)$ are the electron densities of the cluster with and without the hydrogen atom. In $\delta n(r)$ the errors due to the finite size of the cluster will be largely canceled and $\delta n(r)$ approaches to the asymptotic limit much faster than, e.g., $n_{\text{H}}(r)$. In Fig. 6, $r^2 \delta n(r)$ calculated for 3-, 22-, and 92-electron clusters are compared to the exact result of the infinite jellium. The appearing of the Friedel oscillations can be seen already in the result for three-electron cluster and when the cluster increases, more and more oscillations will be reproduced. Already a 22-electron cluster gives a fairly good description of the induced charge density around the proton in jellium.

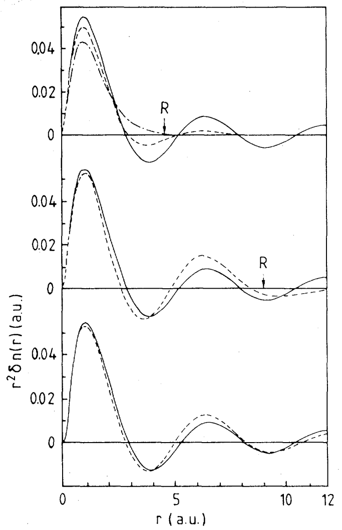

FIG. 6. Radial-electron density around hydrogen for 3-, 22-, and 92-electron clusters (dashed lines). The solid line in each figure indicates the density for an infinite system. The dot-dashed line in the uppermost figure the density of a free hydrogen atom. The cluster radius is denoted by R (for the 92-electron cluster $R = 14.7$ a.u.).

The eigenvalue spectrum of the cluster of 125 electrons and the hydrogen atom is shown in Fig. 1. The hydrogen impurity causes major charges only in the s states which are pulled down so that finally the 2s state replaces the 1s state of the pure cluster and the 1s state forms an impurity bound state slightly below the conduction band. In the infinite jellium this doubly occupied bound state is only 0.009 Hartree's below the bottom of the conduction band. This downward shift of the 1s state has also been observed in other cluster calculations.[6,19]

The total energy of the hydrogen in the electron gas can be determined from the cluster calculations simply by taking the difference of the total energies of the cluster with and without the hydrogen atom. This energy difference is shown in Fig. 7 as a function of the cluster radius. The energy difference

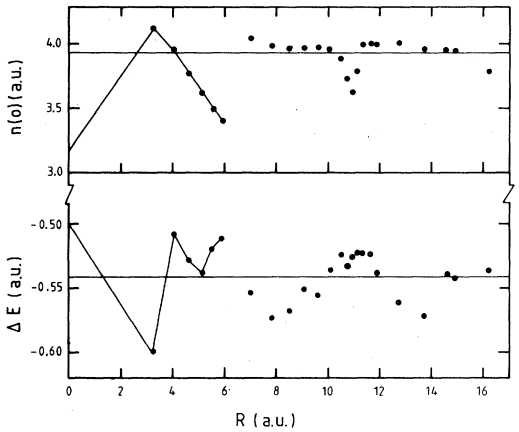

FIG. 7. Contact density at the hydrogen impurity and the hydrogen heat of solution as a function of the cluster radius. The results up to 6-atom cluster are connected with a line. For larger clusters all possible sizes were not studied.

fluctuates around the asymptotic value showing that a large cluster (about 100 electrons) is needed for an accurate description of the hydrogen energy. Figure 7 also shows the contact electron density at the proton. Like the total energy, the contact density may also have large departures from the asymptotic value even for very large clusters. For example, the contact density in the 125-electron cluster is much smaller than the asymptotic value due to the empty 4*s* level just above the Fermi level. When the 4*s* state is filled (139-electron cluster, see Fig. 1) the contact density will be too large. Owing to this population mechanism, this kind of fluctuation as a function of the cluster size can be seen in all calculated quantities.

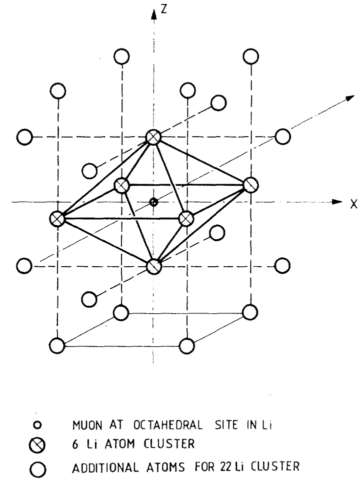

FIG. 8. Geometry of the 22-Li-atom cluster investigated by the unrestricted Hartree-Fock method.

V. SOME HARTREE-FOCK CLUSTER RESULTS

In more realistic cluster calculations, the lattice geometry must also be included. Unfortunately, this increases the computational effort such that only clusters with very few atoms can be handled.

The study of a hydrogen impurity in small Li clusters by means of spin-polarized Hartree Fock (UHF) calculations has been performed in Ref. 6, to which we also refer for more details. In that paper, a 6- and 22-Li-atom cluster with and without a hydrogen in the cluster center was considered. The hydrogen impurity was supposed to be at the octahedral interstitial site as shown in Fig. 8. The energy levels of these UHF calculations do not show the high degeneracy as those of Fig. 1. This is due to the reduction of the cluster symmetry (there is only the fourfold symmetry around the *z* axis). However, as in the jellium cluster, the "1*s* states" are pulled downwards when the hydrogen is in the cluster center. The same fact was also observed in $X\alpha$ calculations where these states were named the hydrogen bonding states.[18]

This kind of cluster calculation allows us to study orientationally dependent effects, which is not possible in the structureless jellium model. The total charge density for the ground state of a 22-Li-atom cluster with and without hydrogen in the cluster center is shown in Fig. 9, where *r* is the distance from the cluster center in the [101] direction. Both Li22 and Li22H clusters were neutral. The first one has 34 spin-up and 32 spin-down electrons, whereas the latter one has 34 spin-up and 33 spin-down electrons. Comparing with the jellium-cluster charge density (Fig. 5), we realize that both models, although very different, yield surprisingly similar charge-density profiles.

The radial-induced electron density around the hydrogen impurity as a function of the radial dis-

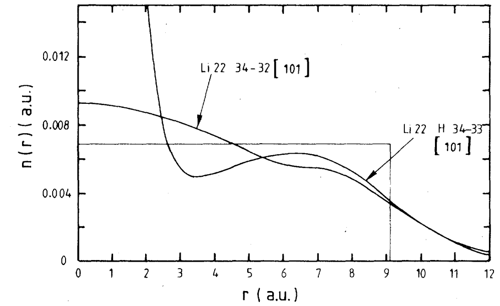

FIG. 9. Hartree-Fock electron density in the 22-Li-atom cluster along [101] direction. The solid line is the result for the pure cluster and the dashed line is the result with the hydrogen impurity in the center of the cluster. The rectangle corresponds to the homogeneous positive jellium background of Fig. 6.

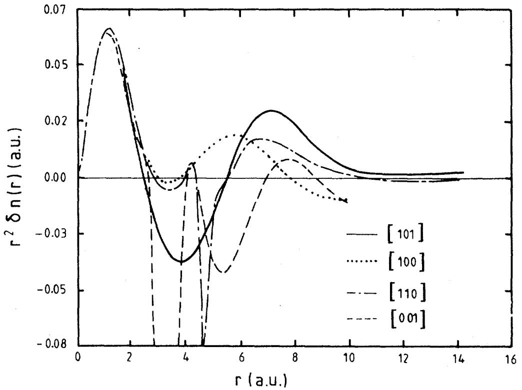

FIG. 10. Radial-induced electron density around the hydrogen impurity along four different directions. The deep minima in the [001] and [110] directions are at the site of the neighboring Li atoms.

tance is shown along four different directions in Fig. 10. In all directions Friedel-type oscillations occur, where the deep minimas of the [001] and [110] directions correspond to the nearest-neighbor and next-nearest-neighbor Li atoms, respectively. We notice that both amplitudes and phases of the oscillations strongly depend on the radial direction. However, the wavelengths are comparable to that of the 22-atom jellium cluster in Fig. 6.

VI. SPIN DENSITY AROUND THE IMPURITY

The ground state of a finite jellium cluster is in general magnetic: If the highest energy level is not completely filled, the ground state maximizes the total spin as in free atoms (Hund's rules). This leads to a nonzero spin-density distribution in the cluster and to an energy splitting between spin-up and spin-down electrons. The magnetism of small metal clusters is an interesting feature as such[10–12] and is the origin of the difficulties in estimating magnetic properties of the bulk metal using the cluster technique.[20] Our special case of interest is the spin-density distribution around a hydrogen impurity in simple metals (jellium), and particularly the contact spin density which gives the major contribution to the Knight shift.

Neglecting the diamagnetic shielding[21] the Knight shift in nonmagnetic metals in a site of a cubic symmetry can be written as

$$K=\frac{H_{\mathrm{hf}}}{H_{\mathrm{ext}}}=\frac{8\pi}{3}\chi_s\rho_s(0)\;, \tag{6}$$

where H_{hf} and H_{ext} are the hyperfine and external magnetic fields, χ_s the spin susceptibility. $\rho_s(0)$ is the spin-density enhancement at the hydrogen site (assumed to be at the origin), defined as

$$\rho_s(r)=[n^{\uparrow}(r)-n^{\downarrow}(r)]/(n_0^{\uparrow}-n_0^{\downarrow})\;, \tag{7}$$

where $n^{\uparrow}(r)$ and $n^{\downarrow}(r)$ are the spin-up and spin-down electron densities in the system with the impurity and $n_0^{\uparrow}-n_0^{\downarrow}$ is the average spin density in the metal without the impurity. In a self-consistent calculation Eq. (7) includes a contribution due to the repopulation of the energy levels and the so-called core contribution arising from small changes of the bound states and the conduction-electron wave functions below the Fermi level. If the latter is neglected $\rho_s(0)$ can be written as[22]

$$\rho_s(0)=V\langle\,|\psi(0)|^2\rangle_{\mathrm{FS}}\;, \tag{8}$$

where V is the normalization volume and $\langle\,|\psi(0)|^2\rangle_{\mathrm{FS}}$ is the square of the wave function at the impurity averaged over all states at the Fermi surface.

In the spin-density-functional method the electron densities are calculated as sums over squares of single-particle wave functions[15]:

$$n_\sigma(\vec{r})=\sum_{\substack{i\\ E_{i\sigma}<E_F}}|\psi_{i\sigma}(\vec{r})|^2\;, \tag{9}$$

where $\sigma=\uparrow,\downarrow$ and the sum goes over all energy states below the Fermi level. In an infinite electron gas the energy states (in the conduction band) form a continuum and the sum in Eq. (9) is replaced by an integral. In this case the spin-density enhance-

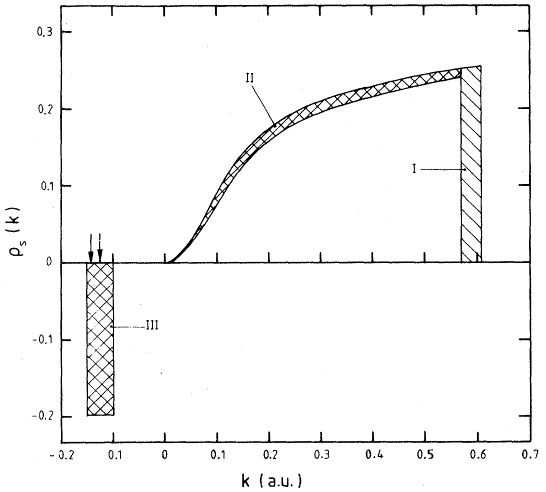

FIG. 11. Partial wave decomposition of the contact electron density at the hydrogen in a polarized ($\zeta_0=0.1$) infinite electron gas ($r_s=3.25$). The upper and lower curves at positive k values give the spin-up and spin-down densities, respectively. The arrows show the binding energies of the bound states ($\epsilon=-\sqrt{2}\,|k|$). The dashed areas give the contact spin density: I, The Fermi-surface contribution; II, the core polarization of the conduction states, and III, the core polarization of the bound state.

ment, Eq. (7), can be calculated by the self-consistent solution of the Kohn-Sham equations in a polarized electron gas (with a small polarization of, e.g., $\zeta_0=0.1$),[23] or by using a self-consistent perturbation theory.[24] The different contributions to the spin density at the hydrogen embedded to an infinite electron gas ($r_s=3.25$) are illustrated in Fig. 11. The contact spin density can be divided into three main terms: the positive Fermi-surface term of Eq. (8), a negative core polarization of the bound states, and a positive core polarization of the conduction electrons. The partial cancellation of the two core polarizations makes the conventional approximation, Eq. (8), to work fairly well for hydrogen in jellium.[25]

In principle, a self-consistent calculation for a polarized cluster with the impurity gives a contact spin density which approaches to the correct value of the infinite jellium when the cluster size increases. However, this direct calculation is in practice not applicable. For example we can study the 125-electron cluster with the hydrogen impurity. The ground state of this cluster is magnetic with a magnetic moment of $12\mu_B$, corresponding to an average polarization of about $\zeta_0=0.1$, the same as in Fig. 11. However, the spin density at the hydrogen site is *negative*. This can be readily understood by noticing from Fig. 1 that there are as many spin-up and spin-down states (s states) below the Fermi level contributing to the electron density at the origin: i.e., all spin density comes from core polarization and the Fermi-surface contribution is missing. By increasing the polarization ζ_0 the 4s spin-up state will be filled resulting to a very large positive contact spin density (too-large Fermi-surface contribution). This example illustrates that owing to the small number of s states a huge cluster size (computationally intractable, especially for the more sophisticated Hartree-Fock calculations) is needed before a direct self-consistent calculation of a polarized cluster correctly describes the spin density at the origin. In actual metal clusters with less symmetry there will be more states contributing to the contact density and the problem will be slightly reduced, but still the $X\alpha$ calculations of Yang *et al.*[10] for 15-atom iron clusters show that the hyperfine field at the central atom is much too negative. Similar findings were also observed in Hartree-Fock Li and Be cluster calculations.[6]

TABLE I. Different contributions to the spin-density enhancement at the hydrogen. N is the number of electrons in the cluster, C_{I} is the core contribution from the lowest-energy state, and C_{II} that of all other states below the Fermi surface. FS is the Fermi-surface contribution.

N	C_{I}	C_{II}	FS	Total
22	−10.1	5.6	15.0	10.5
30	−9.8	5.2	14.3	9.7
34	−16.4	−1.1	14.0	−3.5
50	−15.6	11.7	17.3	13.4
90	−15.8	11.1	14.3	9.6
96	−13.2	8.7	14.2	9.7
∞	−14.4	11.5	14.1	11.1

Although the direct calculation for polarized clusters cannot reproduce the total contact spin density, it can give qualitative understanding of the core polarization as shown in Table I. The contact spin density was calculated for ground states of different polarizations of the cluster, and the spin-density enhancement was determined from the derivative $d[n^{\uparrow}(0)-n^{\downarrow}(0)]/d[n_0^{\uparrow}-n_0^{\downarrow}]$ at the polarization $\zeta_0=0.1$. In columns 1 and 2 of Table I we show the contact spin densities arising from the polarization of the lowest s state (impurity state) and from the polarization of other s states (conduction band), respectively. Already for very small clusters both core contributions are close to the exact asymptotic limits. In the case of the 34-electron cluster there is an s state just above the Fermi level and thus, due to the discreteness of the levels, the contribution of s states to the conduction band is smaller than in the infinite jellium. This leads to a too-small positive core contribution as seen in Table I (column 2). In the cases where the Fermi level stays in the middle of two s states the direct calculation gives good estimates for the core polarizations.

The Fermi-surface contribution can be estimated directly from Eq. (8). In a finite cluster none of the s states is usually at the Fermi energy and for estimating the s-state amplitude, $|\psi_s(0)|^2$, we have used linear interpolation between the highest-occupied and lowest-unoccupied s states. In order to do the averaging over the Fermi surface one has to estimate the s-electron contribution to the density of states, $N_s(\epsilon)$, at the Fermi surface, and one can write

$$\langle |\psi(0)|^2 \rangle_{\mathrm{FS}} = |\psi_s(0)|^2 \frac{N_s(\epsilon_F)}{N(\epsilon_F)} \ . \tag{10}$$

N_s and N can be estimated as (average) derivatives of the integrated density of states. For small clusters this method is fairly inaccurate due to the small number of energy levels. If the electronic structure of the infinite host metal is known one can make use of that and write

$$\langle |\psi(0)|^2 \rangle_{\mathrm{FS}} = \frac{|\psi_s(0)|^2}{|\psi_s^0(0)|^2} \langle |\psi^0(0)|^2 \rangle_{\mathrm{FS}} \ , \tag{11}$$

where $\psi^{(0)}$ denotes the wave function of the (infinite) host without the impurity. If $\langle |\psi^0(0)|^2\rangle_{\rm FS}$ is known for the infinite system, $|\psi_s(0)|^2$ and $|\psi_s^0(0)|^2$ can be calculated for the same cluster sizes with and without the impurity. In this way a cancellation of errors due to the finite size of the cluster is expected. The results for the jellium clusters, using Eq. (11), are shown in Table I and in Fig. 11. Although being in average in good agreement with the exact asymptotic limit, the results again fluctuate strongly with the cluster size in the same way as the contact charge density in Fig. 7.

In small polarized clusters the repopulation of states close to the Fermi level is not evenly distributed among the states of different l values and the resulting spin distribution might be a poor approximation to that in the infinite metal. This means that the exchange-correlation potential has a wrong spatial distribution and may cause large errors in the above estimation of the core polarization. In fact a better approximation for the total spin density might be to apply perturbation theory to a nonpolarized cluster. In an infinite jellium this leads to an integral equation for the magnetization.[24] In the case of a finite cluster one can proceed as follows: In the limit of a small polarization the spin-density distribution is

$$n^{\uparrow}(\vec{r})-n^{\downarrow}(\vec{r})=\zeta_0 N\langle |\psi(\vec{r})|^2\rangle_{\rm FS} + \sum_{\substack{i \\ \epsilon_i<\epsilon_F}} [\,|\psi_{i\uparrow}(\vec{r})|^2-|\psi_{i\downarrow}(\vec{r})|^2]\,, \tag{12}$$

where N is the total number of electrons. The spin density of Eq. (12) causes splitting in the exchange correlation potential, which changes the wave functions. We have solved this self-consistency problem by a direct iteration starting from a nonpolarized solution and determining in each iteration the spin-dependent exchange-correlation potential from Eq. (12) (but keeping the population of states unchanged). The Fermi-surface contribution, first term in Eq. (12), was estimated by linear interpolation of the squares of the wave functions of states below and above the Fermi level (separately for each l value). The resulting total spin enhancement is shown in Fig. 12. Generally, the perturbation method does not given any bettter agreement with the asymptotic limit than in direct calculation of polarized clusters.

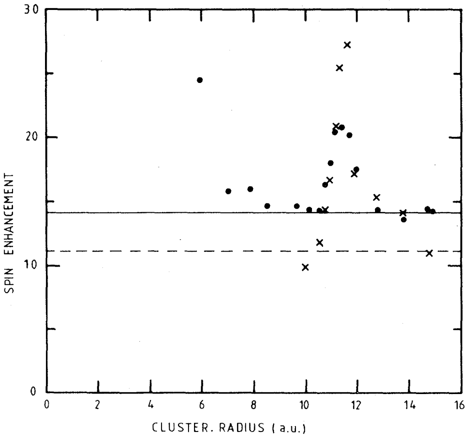

FIG. 12. Spin enhancement at the hydrogen impurity as a function of the cluster radius. The black dots are the Fermi-surface contribution from Eq. (8) and the solid line is the corresponding asymptotic limit. The crosses are the total spin enhancement estimated using the perturbation theory and the corresponding asymptotic limit is denoted by a dashed line.

It should be mentioned that the jellium model is used here only as a model where the limit of the infinite system is exactly known. In calculating the Knight shift of a positive muon (of hydrogen) in simple metals the inclusion of the actual lattice potential (or pseudopotential) is essential.[6,23,26]

VII. CONCLUSIONS

The jellium model provides a good test for the applicability of the cluster calculations in describing the electronic properties of the infinite simple metal. Surprisingly large clusters (more than 100 electrons) are needed for an accurate description of the total energy, band-width, and density of states of the bulk metal. In studying the impurity properties a partial cancellation of errors can be achieved by comparing the results of cluster calculations with and without the impurity, but the finite number of energy levels may still cause large errors. The estimation of magnetic properties of metals or impurities from cluster calculations is more difficult due to the possibility of a magnetic ground state caused by the finite number of energy levels. Results of unrestricted Hartree-Fock calculations for small Li clusters with a hydrogen impurity show the same trend that the results are sensitive to the cluster size.

Moreover, almost all the peculiar features (e.g., polarized ground state, negative spin density in the cluster center) are also observed in Hartree-Fock and $X\alpha$ calculations. Thus, these peculiarities are a consequence of the finite cluster size and not an artifact of approximations of the many-body Hamiltonian (Hartree-Fock, $X\alpha$, jellium). However, a proper embedding of the cluster to an infinite effective medium might give better results for very small clusters.

Our results clearly show that relevant information from cluster calculations can only be obtained if all possibilities are explored (variation of the cluster size, cluster polarization, lattice geometry, etc.) which can only be obtained by considerable computational effort. An agreement with the experimental result obtained from one single-cluster calculation does not guarantee that the physical property is correctly understood.

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