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Electronic structure of hydrogen in simple metals*

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Based on the Hohenberg-Kohn-Sham formalism a fully self-consistent calculation of the electron density distribution around a proton in the metallic density range is presented. The calculation takes into account the first gradient correction to the exchange-correlation potential, hitherto treated only in the local density approximation. Very shallow bound states are found to exist for all metallic densities ($r_s = 2.07-5$) considered. The physical picture regarding the electronic structure of a proton in the metallic density range is that of an extended H^- ion accompanied by an equally extended compensating hole in the uniform electron gas. Assuming that a positive muon (μ^+) constitutes a heavy impurity in an electron gas, the Knight shift at μ^+ site as a function of electron density (r_s) has also been calculated and the results are compared with experiment.

I. INTRODUCTION

Hydrogen in metals forms the simplest and yet the most interesting impurity. Its simplicity stems from the fact that hydrogen upon dissolving in a metal dissociates into a proton and an electron, the former has no electronic "core" structure. It is this latter fact which makes the problem theoretically very interesting. Since the proton provides a very strong perturbing potential to the electron gas, the problem of calculating the screening charge around a proton is a nonlinear one.[1] A somewhat related question concerns the electronic state of hydrogen in the metallic-density range, namely, does a proton remain as a free point charge or does it exist in a bound state with the electrons?

Recently, Popovic *et al.*[2] have calculated the nonlinear electron-density distribution around a proton in a paramagnetic electron gas, using the density-functional formalism of Hohenberg, Kohn, and Sham.[3] These authors were able to obtain approximately self-consistent electron density by parametrizing the effective electron potential. While this work was in progress, a fully self-consistent calculation of this problem has been carried out by Almbladh *et al.*[4] and Zaremba *et al.*[5] All these calculations have beer done in the local density approximation, which is valid for the case of a slowly varying density. In the case of a proton where the electron pile up around it is large and varies rather rapidly, it is *a priori* not clear that the local density approximation is valid.

In this paper, using the Hohenberg-Kohn-Sham (HKS) formalism,[3] we present a fully self-consistent calculation of electron-density distribution around a proton in the metallic density range. We incorporate the first gradient correction to the exchange-correlation potential. We neglect higher-order gradient corrections since they have been shown[6] to be small even for surface density profiles. The question regarding the electronic state of a proton in metals is discussed.

Assuming that a positive muon (μ^+), like a proton, consitutes a heavy impurity in an electron gas, we have calculated the Knight shift at a μ^+ site as a function of r_s (electron density). The results are compared with available experimental data.[7]

II. KOHN-SHAM FORMALISM

For the sake of completeness, we shall here briefly outline the density-functional formalism of Hohenberg, Kohn, and Sham.[3] According to this formalism, one writes the energy functional of the particle density $n(r)$ as

$$E[n(\vec r)] = T_0[n(\vec r)] + e\int d\vec r\, n(\vec r)\, V_{\text{ext}}(\vec r) + \frac{e^2}{2}\int \frac{n(\vec r)\,n(\vec r\,')}{|\vec r - \vec r\,'|}\, d\vec r\, d\vec r\,' + E_{xc}[n(\vec r) \tag{1}$$

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where $T_0[n(\vec{r})]$ is the kinetic energy of a system of noninteracting electrons with the same density $n(\vec{r})$, and $E_{xc}[n(\vec{r})]$ is the exchange correlation energy. The other terms in Eq. (1) have their usual meaning. The true ground-state density is that $n(\vec{r})$ which minimizes $E[n(\vec{r})]$; this minimum being the true ground-state energy.

This variational principle leads to the following set of self-consistent equations (we have used Rydberg atomic units throughout this paper):

$$\{-\nabla^2 + V_{\text{eff}}[n(\vec{r}),r]\}\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \ , \tag{2a}$$

$$n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2 \ , \tag{2b}$$

$$V_{\text{eff}}[n(\vec{r}),r] = \Phi(\vec{r}) + V_{xc}[n(\vec{r})] \ , \tag{2c}$$

where the electrostatic potential

$$\Phi(\vec{r}) = -\frac{e}{r} + e\int d\vec{r}\,' \frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \ , \tag{3}$$

and

$$V_{xc}[n(\vec{r})] = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} \ . \tag{4}$$

In most applications, the local density approximation for $E_{xc}[n(\vec{r})]$ is used, i.e.,

$$E_{xc}[n(\vec{r})] \cong \int d\vec{r}\, n(\vec{r})\epsilon_{xc}[n(\vec{r})] \ , \tag{5}$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy per particle for a homogeneous electron gas of density $n(\vec{r})$; and here, it has been taken from the work of Vashishta and Singwi[8]

$$\epsilon_{xc}(r_s) = -\frac{0.9163}{r_s} - 0.112 + 0.0335\ln r_s - \frac{0.02}{0.1+r_s}$$

In this approximation, we then have

$$V_{xc}[n(\vec{r})] = \frac{d}{dn}[n\epsilon_{xc}(n)] - \mu_{xc}(n_0) \ , \tag{6}$$

where $V_{xc}[n]$ has been defined with respect to the exchange-correlation potential μ_{xc} for the average density n_0 of the host metal. As $r \to \infty$, both $\Phi(r)$ and $V_{xc}(n)$ tend to zero. The local density approximation is certainly valid if the density variation is sufficiently gentle. This is definitely not the situation either at a metal surface or near a proton. Nevertheless, this approximation in the former case has been found[9] to give results in reasonably good agreement with experiment.

III. GRADIENT CORRECTIONS TO EXCHANGE-CORRELATION ENERGY

Exchange-correlation energy of an inhomogeneous electron gas can be expanded[6] in powers of small deviations from the average density, i.e.,

$$E_{xc}(n) = \int d\vec{r}\, n(\vec{r})\epsilon_{xc}[n(\vec{r})] + \frac{1}{2}\int d\vec{r}\, g_{xc}^{(2)}[n(r)]|\vec{\nabla}n(\vec{r})|^2 + \frac{1}{6}\int d\vec{r}\, g_{xc}^{(3)}[n(\vec{r})]\vec{\nabla}n(\vec{r})\cdot\vec{\nabla}[\nabla^2 n(\vec{r})] + \cdots \ , \tag{7}$$

where the first term is the well-known local density term while the second and third terms represent, respectively, the first and second gradient corrections. The coefficient $g_{xc}^{(2)}(n)$ has recently been estimated by Rasolt and Geldart[10] and Gupta and Singwi.[6] The latter authors find that the correction to the surface energy of metal-vacuum interface due to the first gradient term is of the order of +20%, and that due to the second gradient term is negative and amounts to only a few percent. Guided by this fact, we decided to include only the first gradient correction term in the self-consistent calculation of the screening charge around the proton in the HKS formalism. The exhcange-correlation potential then has the form

$$V_{xc}[n(r)] = \frac{d}{dn}[n\epsilon_{xc}(n)] - \mu_{xc}(n_0) - \left[\frac{1}{2}\frac{dg_{xc}^{(2)}}{dn}\left(\frac{dn}{dr}\right)^2 + g_{xc}^{(2)}(n)\frac{d^2n}{dr^2}\right] \ . \tag{8}$$

where the coefficient $g_{xc}^{(2)}(n)$ is given by[6]

$$g_{xc}^{(2)}(n) = -4\pi e^2\beta(r_s)/(3\pi^2 n)^{4/3} \ . \tag{9}$$

Since the electron density in the vicinity of a proton is large (i.e., r_s small), we have used for $\beta(r_s)$ the values given by Rasolt and Geldart,[10] which are exact in the high-density limit $\{\beta(r_s)$ of Eq. (9) is related to $c(r_s)$ of Rasolt and Geldart[10] by $\beta(r_s) = -[(3\pi^2)^{4/3}/2\pi]c(r_s)\}$.

IV. NUMERICAL PROCEDURE

Since the effective electron potential in Eq. (2c) is spherically symmetric, it is convenient to express Eq. (2a) in terms of its radial component,

$$\left[-\frac{d^2}{dr^2} + V_{\text{eff}}(r) + \frac{l(l+1)}{r^2} - k^2\right]U_{kl}(r) = 0 \ , \tag{10}$$

where we have assumed the unperturbed system to be free-electon-like so that the electron wave functions are plane waves and the energy of the electron in state k is k^2. The wave function ψ_l is expressed in terms of its radial component $U_{kl}(r)$ through

$$\psi_l(\vec{r}) = [U_{kl}(r)/r]\, Y_{lm}(\hat{r}) \quad . \tag{11}$$

Thus the electron density in Eq. (2b) can be rewritten as

$$n(\vec{r}) = \frac{1}{\pi^2}\int_0^{k_F} dk\, k^2 \sum_l (2l+1)(U_{kl}(r)/r)^2 \quad . \tag{12}$$

The radial wave function $U_{kl}(r)$ has the well-known asymptotic form at large r, namely,

$$U_{kl}(r) \underset{r\to\infty}{=} \cos\delta_l(\epsilon_k) j_l(kr) - \sin\delta_l(\epsilon_k) n_l(kr) \quad , \tag{13}$$

where δ_l's are the scattering phase shifts for l th partial wave and j_l and n_l are, respectively, spherical Bessel and Neuman's functions of order l. The scattering phase shifts at the Fermi energy satisfy the Friedel sum rule:

$$Z = \frac{2}{\pi}\sum_l (2l+1)\delta_l(\epsilon_F) \quad . \tag{14}$$

Z is the charge of the impurity and is unity in the case of a proton. The factor 2 is due to spin.

For a sufficiently strong potential, there can also exist bound states. The condition for the occurrence of bound states in the lth partial wave is

$$\delta_l(\epsilon_k = 0) = n\pi \quad ,$$

and the number of bound electrons with quantum number l is $2n(2l+1)$. It is worth mentioning that it is energetically favorable for the first bound state to occur in the $l=0$ state. In the present problem, we found the presence of only s-wave bound states. To obtain the bound-state energy as well as the bound-state wave function, one has to solve Eq. (10) for negative energy states. The bound-state wave function ψ_b must then satisfy the boundary condition

$$U_b(r) \sim e^{-k_b r} \quad , \tag{15}$$

with $\psi_b(r) = [1/(4\pi)^{1/2}]\, U_b(r)/r$ and the binding energy, $|\epsilon_b| = k_b^2$.

If one writes the deviation of the electron density around a proton from the average density n_0 as $\delta n(r)$, then including contributions from bound states (if any),

$$\begin{aligned}\delta n(r) &= n(r) - n_0 \\ &= \frac{1}{\pi^2}\int_0^{k_F} dk\, k^2 \sum_l (2l+1)\left[\frac{U_{kl}^2(r)}{r^2} - j_l^2(kr)\right] \\ &\quad + 2\psi_b^2(r) \quad ,\end{aligned} \tag{16}$$

with the normalization requirement that

$$\int d^3r\, \psi_b^2(r) = 1 \tag{17}$$

Thus, given an initial potential, one solves Eq. (10) for $U_{kl}(r)$ for k ranging from 0 to k_F and all values of partial waves. In practice, we have divided the interval from 0 to k_F in twenty segments and l from 0 to 14. The radial wave functions are matched to the asymptotic form in Eq. (13) for $r \geqslant 19.5a_0$ [beyond which $V_{\text{eff}}(r)$ was set equal to zero] and $n(r)$ is computed from Eq. (12). Calculations were repeated for different choices of the cut off radius ($r > 19a_0$), and it was found that the corresponding values of $n(r)$ did not differ by more than 0.1% (the accuracy claimed in the convergence procedure). The electrostatic part is then computed from this new charge density by solving the Poisson's equation,

$$\nabla^2\Phi(\vec{r}) = 4\pi e[\delta(\vec{r}) - \delta n(\vec{r})] \quad , \tag{18}$$

where the proton is situated at the origin. The exchange-correlation potential is computed from both Eqs. (6) and (8). In each iteration, the Friedel sum rule has to be satisfied. The process is repeated until self-consistency in the electron-density distribution is achieved. Although in principle it is a simple procedure, the main difficulty in obtaining a self-consistent solution is a numerical one. For this scheme to work, it is necessary to demand an unreasonably high accuracy in the Friedel sum rule of Eq. (14). A small violation of this rule leads to a small amount of charge δZ which has a long Coulomb tail. In subsequent iterations, this leads to a divergent result. To overcome this difficulty, Popovic *et al.*[2] chose to parametrize the electrostatic potential using two parameters and obtained an approximate self-consistent solution for the charge density. Zaremba *et al.*[5] have extended the accuracy of the results by taking ten parameters to represent the electrostatic potential.

We have followed a numerical procedure suggested by Manninen *et al.*[11] where no such parametrization is necessary. In this method, one rewrites Eq. (18) as

$$\nabla^2\Phi - k_{\text{TF}}^2\Phi = 4\pi e[\delta(\vec{r}) - \delta n(r)] - k_{\text{TF}}^2\Phi \quad , \tag{19}$$

which has a recursive solution,

$$\Phi^j(r) = -\int d^3r'\, \frac{e^{-k_{\text{TF}}|\vec{r}-\vec{r}\,'|}}{4\pi|\vec{r}-\vec{r}\,'|}\{4\pi e^2[\delta(\vec{r}\,') - \delta n^{j-1}(r')] - k_{\text{TF}}^2\Phi^{(j-1)}(r')\} \tag{20}$$

where j and $j-1$ correspond to the number of iterations and k_{TF} is the Thomas-Fermi screening constant. Note that Eq. (20) is mathematically correct when $\Phi(r)$ is self-consistent, i.e., $\Phi^j(r) = \Phi^{j-1}(r)$. The advantage of this procedure is that the nonzero Coulomb tail at large r, that would normally exist if the Friedel sum rule is not satisfied, gets truncated due to the exponential term in Eq. (20).

Using this procedure, we were successfully able to achieve self-consistency in electron density to better than 0.1% at small r. The convergence at large r was much better. In the high-density limit ($r_s \sim 2$), it was sufficient to perform about 20 iterations whereas for low density ($r_s \sim 5$) to achieve the same kind of accuracy, we had to go beyond 30 iterations. We found that it is not the singular nature of the electrostatic potential in Eq. (3) that causes the solutions not to converge, but the difficulty lies in the effective potential not being zero at large r due to numerical inaccuracy.

V. ELECTRON DENSITY DISTRIBUTION AND BOUND STATES

We shall first discuss our results of the electron distribution around a proton in both local density approximation and including first gradient correction. The question of formation of bound states will be taken up in the latter part of this section.

The electron distribution normalized to the mean density n_0 of the homogeneous background is plotted in Fig. 1 for the density range $2 < r_s \leq 5$. We note that the electron pile up increases sharply as r_s increases. In the inset of Fig. 1 are shown the Friedel oscillations. The amplitudes of these oscillations are larger for lower density, which reflect the large pile up of electrons at the origin. The electron distribution for $r_s = 2.07$ (Al density) is in very good agreement with the calculation of Popovic *et al.*,[2] except that the amplitudes of the Friedel oscillations in the present calculation are slightly bigger.

In order to assess the influence of the first gradient correction on the electron-density distribution, we have repeated the calculation for $r_s = 2.07$ and 5 using for $V_{xc}[n]$ the expression in Eq. (8). The results are compared with the local density approximation for $r_s = 5$ in Fig. 2. The electron density in the vicinity of the proton with the first gradient correction is enhanced by about 15% over the corresponding result in the local density approximation. The differences at large r are no more than (2–3)%. As expected, the gradient correction affects the electron density for $r_s = 2$ much less, namely, it leads to an enhancement of about 2% in the electron density at small r. To illustrate this point further, we have compared the exchange-correlation potential in the local density approximation with the first gradient correction for $r_s = 5$ in the inset of Fig. 3. Although the gradient term is a very small fraction of the exchange-correlation potential, its effect on $n(r)$ is not negligibly small at small r. It is, however, encouraging to note that the local density approximation does not underestimate appreciably the electron-density profile even for $r_s = 5$, where $n(r)$ varies rather rapidly with r. These results combined with recent calculations of surface profiles[6] give us added confidence that the HKS formalism[3] even within the local density approximation can provide reliable quantitative results.

Some comments regarding the relevance of gradient corrections are appropriate at this stage. Almost all *a priori* calculations of $g_{xc}^{(2)}(n)$ have shown that it is a positive quantity and the inclusion of the first gradient correction in the calculation of surface energy of metals has a significant effect and in the right direction. On the other hand, for atoms a negative $g_{xc}^{(2)}(n)$ is ap-

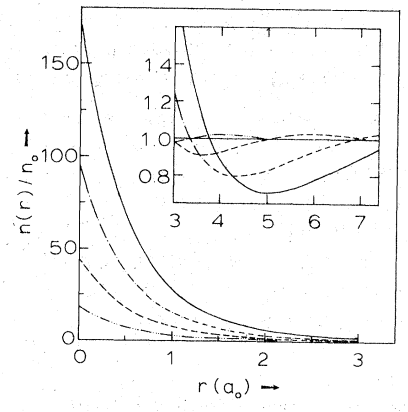

FIG. 1. Normalized electron-density distribution $n(r)/n_0$ around a proton in electron gas. ·········· ($r_s = 2.07$); ----- ($r_s = 3$), -------- ($r_s = 4$) and – ($r_s = 5$). In the inset are shown the Friedel oscillations on a magnified scale.

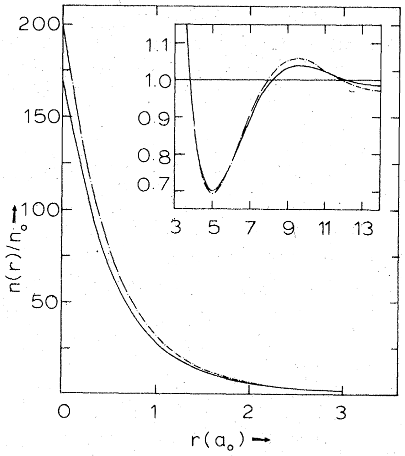

FIG. 2. Electron-density profiles around a proton for $r_s = 5$; – local density approximation, ------- including first gradient correction to exchange-correlation potential. The corresponding Friedel oscillations are magnified in the inset.

parently needed to improve upon the local density results, as found by Herman *et al.*[12] In view of this, one might worry about the significance of gradient corrections in the present problem. Since the bound states in this problem are extremely shallow, it is reasonable to take for $g_{xc}^{(2)}(n)$ the values which are calculated for an inhomogeneous interacting electron gas. For atoms or ions no *a priori* calculations of $g_{xc}^{(2)}(n)$ exist at present. The problem of H^- ion in the Kohn-Sham theory and its relationship to the infinitely dilute limit ($r_s \rightarrow \infty$) is of interest. This problem is now being considered in detail by Shore and coworkers.

We now turn to the question: Does the proton exist in a bound state with electrons in the metallic density range and if so, what is its electronic structure? During the course of our numerical self-consistent calculation, we found that bound states exist for all metallic densities ($r_s = 2.07-5$) considered. The convergence in our binding energies was not as good as that in the electron density and potential. In the local density approximation, the binding energies, for example, at $r_s = 2.07$ and 5 are 0.000 35 and 0.016 Ry, respectively. With the first gradient correction taken into account, the binding energy of the electron at $r_s = 5$ decreases to about 0.001 Ry, while this has only a small effect on the electron-density distribution. These binding energies [as obtained by solving Eq. (2a) for negative energy values with the boundary condition in Eq. (15)] are indeed tiny as compared to 1 Ry in a hydrogen atom.

The total perturbed electron density can be written as a sum of the scattering and bound-state contributions:

$$\delta n(r) = \delta n_{sc}(r) + \delta n_b(r) \quad . \tag{21}$$

Conservation of charge requires that $\int \delta n(r)\, d^3r = 1$. There are two electrons in the bound state ($\int \delta n_b(r)\, d^3r = 2$) as required by Eqs. (16) and (17). We find that, in this case, the scattering charge density integrates to yield -1, i.e.,

$$\int \delta n_{sc}(r)\, d^3r = -1 \quad ,$$

which ensures the validity of Eq. (21). The total charge of the proton is screened within a distance of two Bohr radii, whereas the bound-state wave function, due to shallow binding, extends over a much larger region $\sim 20a_0$.

In Fig. 4, we have shown the contributions of the scattering and bound-charge densities to the screening charge $Z(R)$ contained in a sphere of radius R for various r_s values. For all densities, the proton is screened within a radius, $R \simeq 2a_0$. Within this screening radius, the contribution of bound-charge densities to the proton screening increases steadily with r_s. For example, at $r_s = 2.07$, bound state contributes only 25% of the screening, whereas this amounts to 80% of the screening charge for $r_s = 5$. For large R, $Z(R) \rightarrow +2$ for bound states for -1 and for scattering states—as it should. It is also of interest to note that the electron density at the proton site $n(0)$ approaches the limiting value of $(1/\pi)a_0^{-3}$ for a hydrogen atom as r_s increases. In the local density approximation $n(0) = 0.519$, 0.394, 0.351, and $0.323a_0^{-3}$ for $r_s = 2.07$, 3, 4, and 5, respectively. When gradient

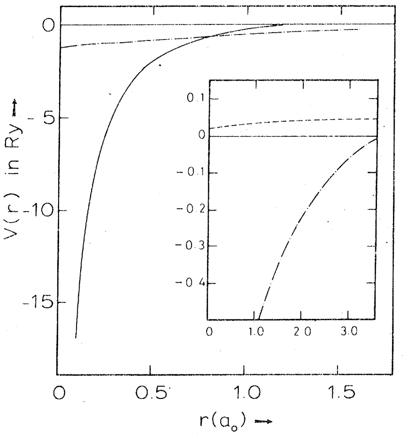

FIG. 3. Comparison between electrostatic (–) and exchange-correlation potential (-------) in the local density approximation for $r_s = 5$. The first gradient correction (----) to the exchange-correlation potential is compared with its local density value in the inset.

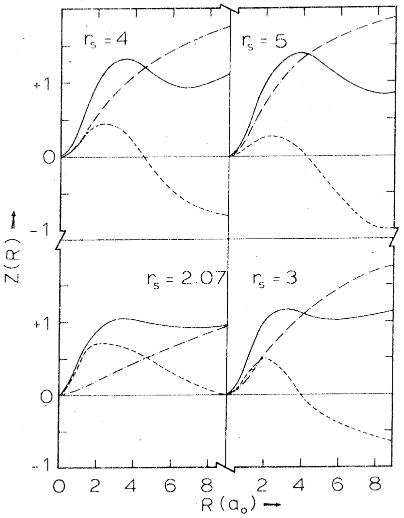

FIG. 4. Screening charge of a proton due to bound (-------) and scattering states (--------). The solid line represents the total screening charge within a radius R (a.u.).

corrections are included, one has to go to larger r_s values for $n(0)$ to approach its limiting value of $(1/\pi)a_0^{-3}$ as is expected from a weaker binding.

The physical picture regarding the electronic structure of a proton in the metallic density range that emerges from our calculation is that of a very extended H^- ion accompanied by an equally extended hole in the continuum. Since in the HKS formalism,[3] the quantity which has a physical significance is the ground-state electron density, one might wonder about the physical relevance of these bound states. This question has been discussed by Almbladh *et al.*[4] They have pointed out that the life time broadening[13] of the single-particle states below the continuum due to electron-electron interactions is larger than the corresponding binding energy. Thus no distinction between these shallow bound states and incipient bound states can be made. Furthermore, the interaction of these extended bound states with the ionic cores of the lattice (neglected in the present calculation) would tend to make the bound states less stable. These bound states should, therefore, be viewed more as resonant states.

VI. KNIGHT SHIFT AT μ^+ SITES

Recently, positive muons created in an anisotropic parity violating decay of π^+ mesons have been used to probe the electronic structure of condensed matter. Internal fields measured at μ^+ sites have been analyzed to provide information regarding the magnetic coupling of the muon spin with the spin-polarized conduction electrons in ferromagnetic metals.[14] The complicated band structures of ferromagnetic metals make a quantitative theoretical understanding of this hyperfine interaction difficult.

A related quantity, Knight shift in paramagnetic metals, measures the electron spin density at the muon site. A positive muon is about 200 times heavier than an electron. Assuming that a positive muon can be treated, like a proton, as a static point charge in an electron gas, the results of the electron distribution around a proton in the present calculation can be used to predict Knight shift values at μ^+ sites in metals. This assumption is supported by a recent experiment[15] on Knight shift at μ^+ site in Pd which turns out to be the same as that on the proton site.

There are several contributing mechanisms to Knight shift of which the Fermi-contact term and exchange-core polarization are the most dominant ones. The former is due to the interaction of the nuclear spin with the polarized conduction electrons, through the Fermi-contact term; and the latter is due to the interaction between the nuclear spin with exchange-polarized core electron orbitals of the ion. Since μ^+ is a point charge and does not have any such conventional core structure in metals, this contribution is zero. The contact part of the Knight shift K at a μ^+ site is given by

$$K = \tfrac{8}{3}\pi\chi_s|\psi_F(0)|^2 ,$$

where χ_s is the paramagnetic susceptibility. $|\psi_F(0)|^2$ is the density of the electrons on the Fermi surface at a μ^+ site. It is to be noted that only $s\,(l=0)$ electrons contribute to the density at the origin.

The Pauli susceptibility χ_s can be measured. However, due to experimental difficulties, only a few metals have so far been studied. This quantity can be estimated from theoretical calculations. Since both band structure as well as many-body effects influence the value of χ_s, its accurate determination from a theoretical point of view is rather difficult. Vashishta and Singwi[16] have calculated χ_s for the metallic density range by including the exchange enhancement due to many-body interactions and neglected the effect of the periodic lattice. Their results agree reasonably well with the experimental values for the alkali metals. Using their results for the exchange enhancement, η and the present self-consistent electron densities at $r=0$ due to s electrons on the Fermi surface, the Knight shift values for $r_s = 2.07$, 3, 4, and 5 are given in Table I.

The Knight shift at a μ^+ site in any metal can be obtained by interpolating the results in Table I. Thus for Mg($r_s=2.65$), Li($r_s=3.26$), Pb($r_s=3.70$), Na($r_s=3.93$), and K($r_s=4.86$), the theoretical value for Knight shift in ppm units are, respectively, 116, 135, 151, 158, and 181; the corresponding experimental values of Hutchinson *et al.* are 86.8, 10.96, 132, 79, and 89.9 ppm, respectively. Apart from Li, the results are in semiquantitative agreement with experiment.

TABLE I. Knight shift (in ppm) at a μ^+ site in simple metals.

r_s	χ_s [a] (cgs vol. units)	$\lvert\psi_f(0)\rvert^2$ (inverse vol. units)	Knight shift (ppm)
2.07	1.68×10^{-6}	7.38	104
3	1.25×10^{-6}	11.97	125
4	1.06×10^{-6}	18.40	163
5	0.95×10^{-6}	23.14	184

[a] Includes the factor due to exchange enhancement.

At this point it is of interest to compare the present results on Knight shift with an earlier calculation by Meier.[17] The latter author adopted an effective electron potential of the Hulthen form $-\lambda e^2/(e^{\lambda r}-1)$, where the parameter λ was determined using the variable phase function approach. Using the s-wave density at the origin calculated from this potential by Meier and the present exchange-enhanced Pauli susceptibility, the Knight shift values for Mg, Li, Na, and K are, respectively, 112, 136, 167, and 224 ppm, respectively. These results are rather in good agreement with our present calculation. The reason for this agreement is that the electron density at small r (which is predominantly due to s waves) is largely determined by the singular electrostatic potential. The exchange-correlation part of the potential for $r < a_0$, as shown in Fig. 3 for $r_s = 5$, forms only a small fraction of the total potential. However, for large r this forms a significant part of the potential and thus $n(r)$ [and other electronic properties depending on the behavior of $n(r)$ at large r], using the Hulthen potential (which does not contain contributions from exchange correlation), is likely to be inaccurate.

The discrepancy in the Knight shifts between theory and experiment could be due to several reasons: (a) contributions from other mechanisms not considered here and (b) neglect of band-structure effects. Periodicity of the lattice usually introduces higher angular momentum components to the electron wave function. This would lower the Knight-shift values obtained here. Since alkali metals are known to be free-electron-like and for which a jellium model is a good approximation, it is surprising that our results for Na and K differ almost by a factor of 2 from experiment.[7] It should be kept in mind that the experiments of Hutchinson *et al.*[7] were not specifically designed to measure Knight shifts, and Schenk[14] in a recent review article has cautioned the reader in taking these experimental values too seriously. Conclusive experiments are definitely needed.

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