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Nuclear Contact Densities for Electrons in Sodium†

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Nuclear contact densities for electrons in atomic and metallic sodium are calculated from the Kohn-Sham self-consistent scheme. The effect of pressure on the nuclear contact density for metallic sodium is also calculated, and the results are in good agreement with the experimentally observed pressure dependence of the Knight shift in sodium.

It is well known that the nuclear contact density of an atom P_A, arising from that part of the wave function where the s electron is essentially in contact with the nucleus,[1] is proportional to the hyperfine splitting by the Fermi relation.[2] The nuclear contact density in a metal P_F is related to the Knight shift K,[3] by

$$K=\Delta H/H=\tfrac{8}{3}\pi\Omega\chi_s P_F\ , \qquad (1)$$

where χ_s is the paramagnetic spin susceptibility and Ω is the volume of the Wigner-Seitz cell. The nuclear contact density P_F is now the density of the conduction electron at the nucleus averaged over the Fermi surface.

Recently we have completed *a priori* calculations on atomic systems[4] and on metallic sodium,[5,6] using the local-effective-potential approximation of the Kohn-Sham self-consistent scheme.[7,8] It was observed there that the electron densities obtained from the scheme were excellent, even though the energies were less accurate.[4,7] Here we use the local-effective-potential approximation of the scheme to calculate the nuclear contact density P_A of sodium atom and compare the result with the observed value from hyperfine interaction. We also calculate the nuclear contact density P_F of metallic sodium at various pressures. The results are compared with quantities inferred from Knight-shift measurements and theoretical estimates of spin susceptibilities at these pressures. In all our nuclear-contact-density calculations, full self-consistency among all electrons has been attained. We do not fix the ion core of metallic sodium to be the same as the ion core of the free atom.

In our previous papers,[4-6] physical quantities related to the total electron density and the total energy of various interacting systems have been calculated and examined. In the calculation of nuclear contact density, we want the self-consistent single-electron wave function of the equivalent one-electron Schrödinger equation which is given explicitly by Eq. (1) of Ref. 4 for atomic systems, and by Eq. (3) of Ref. 6 for metallic sodium. The association of the single-electron eigenvalue at the Fermi level of the equivalent Schrödinger equation with the electron at the Fermi level has been proved by theoretical considerations.[8]

It is easy to include correlation effects among all electrons in the Kohn-Sham scheme. In Ref. 4, we found that in atomic systems the correlation effect is overestimated in the local-effective-potential approximation. This difficulty related to the discreteness of the excitation levels above the ground state should not be serious in the metallic sodium case.[6,9]

There are also difficulties in using the local-effective-potential approximation of the Kohn-Sham scheme to calculate the nuclear contact densities. The local-effective-potential approximation we used is based on the gradient expansion of the electron density. Near the nucleus, rapid variation in density limits the accuracy of the results. But as argued by Kohn and Sham,[7] because this region is a high-density region, the effects of ignoring the gradient terms are not too serious. Another apparent difficulty is the following. It has been shown that in the Hartree-Fock scheme, the exchange polarization of the core electrons by the valence electron also contributes to the nuclear contact density P_F. This has been termed "core polarization."[10-13] Adding the "core-polarization" contribution is therefore an attempt to take account of the correlations neglected in a Hartree-Fock calculation. Correct evaluation of the correlation effects among electrons of different spins will give us this value.[11] Although all correlation effects have been included in the present calculation in an approximate way, we do not distinguish between the spins. The bases of the Kohn-Sham self-consistent scheme are the Hohenberg-Kohn theorems[14] which do not separate the up-spin wave function from the down-spin wave functions.

Further description and discussion of the method can be found in the original papers.[4-9,14] Here we shall only present the results of the calculation.

In Table I, we list values of the valence contribution P_A^V, and the core polarization contribution P_A^C, to the total nuclear contact density P_A in atomic sodium. The result obtained by Brooks and Ham,[15] using the quantum-defect method is considerably larger than that of Kjeldaas and Kohn,[16] who used the empirical Prokofjew potential.[17] It is known

TABLE I. Nuclear contact density P_A in atomic sodium (in a_B^{-3}).

	P_A^V	P_A^C	P_A
Empirical calculation			
Brooks and Ham[a]	0.8402	···	0.8402
Kjeldaas and Kohn[b]	0.685		0.685
Hartree-Fock calculation			
Hartree and Hartree[c]	0.497	···	0.497
Mann[d]	0.527	···	0.527
Cohen *et al.*[e]	0.671[f]	0.037	0.708
Goodings[g]	0.5667	0.0847	0.6514
Present calculation	0.788	···	0.788
Experiment[h]			0.751

[a] Reference 15.
[b] Reference 16.
[c] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A193, 299 (1948).
[d] Reference 18.
[e] Reference 10.
[f] Reference 19.
[g] Reference 20.
[h] References 21–24.

that both empirical calculations give good energy levels of sodium atom in agreement with measured values. The fact that their P_A values differ so much indicated that their single-particle wave functions are less dependable. In these empirical calculations core polarization has not been estimated. Among the Hartree-Fock calculations, the value obtained by Mann[18] is the most recent and perhaps the most accurate. Cohen *et al.*[10] have made an estimate of the core polarization for sodium atom. The estimate by Nesbet[11] is very close to this and we have not put the value in the table. The calculation of Cohen *et al.* is based on the less accurate wave functions of Fock and Petrashen.[19] Their core-polarization estimate include only the *s* electrons. If we add their P_A^C value of 0.037 to the Mann value of P_A^V, the total P_A for Hartree-Fock theory with core polarization is 0.564 instead of the 0.708 given by Cohen *et al.* A later calculation by Goodings[20] gives the value 0.0847 for the total core-polarization contribution of the *s* and *p* electrons. His value of P_A is 0.6514. In our *a priori* calculation including correlation in an approximate way (local effective potential), but not including the core polarization in an explicit way, the value P_A obtained is 0.788. Experimental measurements seem to agree well to give the value 0.751[21–24] for P_A.

In Table II, various calculations of the conduction-electron contribution P_F^V, and the core-polarization contribution P_F^C, to the total nuclear contact density P_F for metallic sodium are listed. Brooks's[17] value is again higher than the Prokofjew-potential value of Kjeldaas and Kohn.[16] The effective potential V_{eff} obtained from our *a priori* calculation can be regarded as a crystal potential. It is compared with the Prokofjew potential in Table II of Ref. 9. They do not differ too much. Perhaps these results indicate that the quantum-defect calculation of Brooks gives relatively less-reliable single-particle wave functions especially at the nucleus. By including the effect of the Hartree field due to the other conduction electrons, Moore and Vosko[12] found a large reduction in P_F^v in the Prokofjew-potential calculation. The effect of core polarization is estimated in the first-principles calculation of Cohen *et al.*[10] who took it to be the same as that in the free atom. Recent values by Mahanti and Das using one-orthogonalized-plane-wave (OPW) calculation and many-OPW calculation are considerably higher.[13] In their estimate all core electrons have been included. For a detailed discussion of their work see Ref. 27. It may be questioned whether OPW calculation can give good wave functions at the nucleus, but their values certainly indicate that core polarization is an important addition to the Hartree-Fock result. The experimental value of 0.509 in Table II is obtained from Eq. (1) by substituting the best experimental values available to date on metallic sodium: The Knight shift is 1.12×10^{-3} cgs units,[28,29] the equilibrium Wigner-Seitz sphere $r_s = 3.93$,[30] and the spin susceptibility χ_s is 1.03×10^{-6} cgs units.[31] Our value of 0.5085 compares well with the measured quantity. In the table, we also list ξ, the ratio of P_F/P_A for sodium from various calculations.

As it has been said above, we have not included the core polarization in an explicit way because we do not distinguish the up-spins from the down-spins in our calculation. We cannot directly take the estimate of Goodings[20] or that of Mahanti, Ferlik-

TABLE II. Nuclear contact density P_F in metallic sodium (in a_B^{-3}).

	P_F^V	P_F^C	P_F	ξ
Empirical calculation				
Brooks[a]	0.664	···	0.664	0.790
Kjeldaas and Kohn[b]	0.555	···	0.555	0.81
Moore and Vosko[c]	0.4476	···	0.4476	0.6644
First-principles calculation				
Cohen *et al.*[d]	···	0.037	···	···
Micah *et al.*[e]	0.623	···	0.623	···
Mahanti and Das[f]				
one OPW	0.5817	0.1487	0.7304	···
many OPW	0.3644	0.0953	0.4597	···
Present calculation	0.5085	···	0.5085	0.6456
Experiment[g]			0.509	0.678

[a] Reference 25.
[b] Reference 16.
[c] Reference 12.
[d] Reference 10.
[e] Reference 26.
[f] References 13 and 17.
[g] References 23, 24, 28, 29, and 31.

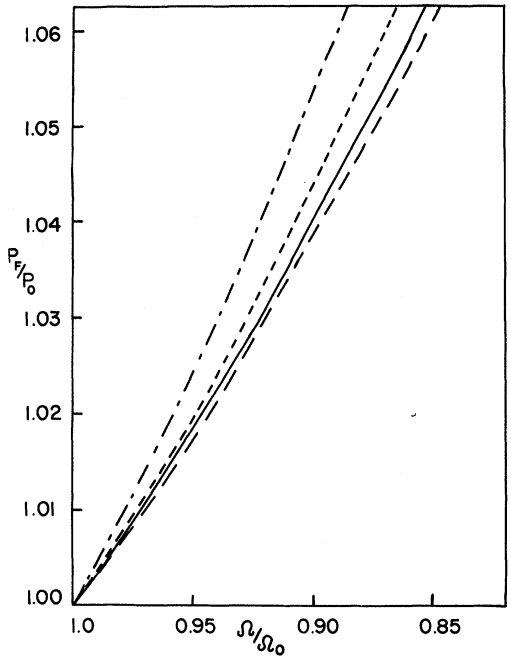

FIG. 1. Theoretically calculated and experimentally deduced volume dependence of P_F/P_0 for sodium. P_F is the nuclear contact density at volume Ω, and P_0 is the nuclear contact density at the equilibrium volume Ω_0. Present calculations (——); deduced from experiments in Ref. 32 (----); Brooks theoretical value as quoted in Ref. 25 (------); deduced from experiments using a pseudopotential as in Ref. 34 (———).

kis, and Das[27] and add to our P_A^V to get P_A^V or to our P_F^V to get P_F. Their estimates are based on the Hartree-Fock scheme. The core-polarization contribution comes from the correlation effects.[11] The inclusion of correlation effects in an approximate way here in our calculation should have included part of the so-called "core-polarization" effect in the Hartree-Fock scheme. Direct additions of their estimates to our P_A^V and P_F^V would overestimate the true core-polarization contribution. In Tables I and II, we take P_A to be the same as P_A^V and P_F to be the same P_F^V in our results. (As a check let us add the estimate of Goodings to our values of P_A^V and P_F^V. The new P_A and P_F are too large compared to experimental values as expected from the overestimation of the core polarization, but they are still comparable to the best theoretical estimates of others as shown in the tables.)

A test of the nuclear contact density, calculated by the present scheme, would be to see how it changes with atomic volume. This can be compared with the experimentally observed variation inferred from the Knight-shift measurements at various pressures. The results of such a calculation are plotted in Fig. 1. The results of Brooks, as quoted by Benedek and Kushida,[31] are also shown. Variation of P_F/P_0 with volume changes cannot be obtained directly from Knight-shift measurements. P_0 is the nuclear contact density at atmospheric pressure and equilibrium volume Ω_0. The change in spin susceptibility with pressure must be taken into account. Benedek and Kushida derived the variation in P_F/P_0 (shown as dot-dashed curve in Fig. 1) by using Pines's theoretical[33] expression for the correlation energy of the electron gas and accounted for the presence of the ions by using effective masses derived from Brooks calculation. We have seen that when χ_s is calculated[34] using a pseudopotential to represent the effect of the ions, it leads towards a better agreement with the experimental values for alkali metals. The results of using such a scheme for χ_s and the measured values of Knight shift to infer the ratio P_F/P_0 is shown by the dashed curve in Fig. 1. We see that the P_F/P_0 obtained from the Kohn-Sham scheme (shown by the continuous curve in Fig. 1) is very close to the dashed curve. *A priori* calculation of spin susceptibility can be made based on the Kohn-Sham scheme,[35] but the use of pseudopotential method is the easiest one to calculate the volume effect on χ_s. More meaningful comparison can be made only after we have direct experimental values of χ_s as a function of volume changes.

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de Haas–van Alphen Effect in Iridium[†]

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Measurements of the de Haas–van Alphen (dHvA) extremal areas have been performed in three main symmetry planes of an Ir single crystal using magnetic fields up to 120 kG. A newly designed modulation-technique magnetometer was used in modulation and sample-rotation experiments; some measurements used the torque technique. Large torque or magnetization oscillations were observed from all four closed sheets of the Fermi surface predicted by the band-structure calculations of Andersen and Mackintosh. The measured cross-sectional areas of two hole sheets centered at X in the Brillouin zone and called $X3$ and $X4$ were found to be, respectively, 30% smaller and 6% larger than the calculated ones. The observed areas of two electron sheets centered at Γ were larger than the calculated ones by not more than 0.5%. The results agree with magnetoresistance data, confirming that Ir is an uncompensated metal and that its Fermi surface does not support open orbits. A few effective-mass values were determined from torque and modulation measurements of the temperature dependence of the amplitude of dHvA oscillations in magnetic fields up to 21 kG. A simultaneous determination of effective masses associated with two dHvA frequencies beating with each other was obtained. A spin-splitting zero was observed in the $\Gamma 6$ sheet in the (111) plane. The Dingle temperature was determined from the magnetic field dependence of the amplitude of torque oscillations. A generalized formula describing the magnetoresistance of an uncompensated metal was used to calibrate a copper-wire magnetoresistor for magnetic field measurements.

I. INTRODUCTION

Iridium and its face-centered-cubic (fcc) neighbors in the Periodic Table, Rh, Pt, and Pd, have recently been studied with the aim of explaining some of their unusual properties. There is considerable interest in the observed weakening of superconductivity towards the end of the sequence Ir, Rh, Pt, Pd, as well as an increasing tendency toward ferromagnetism.[1] Also, the temperature dependence of the resistivity of dilute alloys of these metals with ferromagnetic impurities[2,3] is unusual. This has recently been described using a simple model for scattering of conduction electrons from localized spin-density fluctuations[4,5] in the *d* band resulting from a local increase of the intra-atomic Coulomb potential around the impurities. However, it is still unclear how much the local fluctuations in the spin density and how much the band structure affect the weakening of superconductivity.[6] For either case an accurate knowledge of the existing Fermi surfaces of the involved transition metals constitutes basic information for a quantitative explanation of such effects. While