turned out to be another transition of the F_A center. Nor should the center be confused with those responsible for the B band in silver- and in thallium-doped KCl.

[7] I. Schneider, Phys. Rev. Letters 16, 743 (1966), and Solid State Commun. 4, 569 (1966).

[8] This stability does not include the interconversions that occur between these centers and their primed center (F', F_A', etc.) forms. This was a relatively minor complication since the primed centers are easily eliminated by subsequently exposing the crystal to infrared light and thereby restoring the uncharged forms.

[9] This configuration has been suggested by Lüty (see Ref. 3) as a possible model of the B center primarily because it has the required ⟨100⟩ symmetry.

[10] For a discussion of the evidence for the M-center model, see W. D. Compton and H. Rabin, Solid State Phys. 16, 121 (1964).

[11] The least-squares value of the slope was 1.08.

[12] Lüty has established the ⟨100⟩ symmetry of the center (see Ref. 3) without specifically identifying the transition moment directions of its absorptions.

[13] The bleached centers can subsequently be regenerated by exciting with light in a spectral range closer to the F peak.

MAGNETIC POLARIZABILITY OF CLOSED SHELLS

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The polarizability of closed atomic shells near field inhomogeneities is discussed in connection with several problems of physical interest. We find that magnetically "neutral" $S=0$ atoms or closed shells are attracted and polarized by magnetic field gradients. The effect is demonstrated through sample calculations for noninteracting as well as for interacting electrons.

The helium atom having total spin $S=0$ and angular momentum $L=0$ is generally presumed not to respond to externally applied magnetic fields, the ground state being an eigenstate of the interaction Hamiltonian belonging to eigenvalue precisely zero. The purpose of this note is to point out that closed shells of arbitrary atoms and molecules, as well as noble gases, have their energy lowered in a spatially inhomogeneous magnetic field as a consequence of electronic spin paramagnetism. Inhomogeneous exchange splitting provides a qualitatively similar but markedly stronger mechanism that should be a source of attraction of noble gases to the surface of ferromagnetic metals. A different application of the mechanism under consideration is to the Knight shift in superconductors.[1] The Meissner effect is a mechanism causing inhomogeneity in the magnetic field, in the superconducting state only, and the consequent polarization of closed shells can result in polarizing nuclei via hyperfine coupling. This mechanism is lacking in the normal state, in which case the closed shells are magnetically inert, as described in the opening remarks.

The magnitude of the effect we describe should be orders of magnitude smaller than the spin paramagnetism of paramagnetic atoms, and it should be independent of temperature instead of obeying a Curie law. In these respects it is similar to Van Vleck's temperature-independent orbital paramagnetism which, it has been estimated,[2] might be responsible for a third of the Knight shift in Sn. Inhomogeneous exchange splitting may be many orders of magnitude larger than Van Vleck's mechanism.

The actual calculation of the response of closed shells to inhomogeneous fields is straightforward. The field is decomposed into Fourier components $h(q)$ and the perturbation, for a two-electron system, is separated into singlet and triplet components, as follows:

$$H' = \sum_q h(q)[S_{1z}e^{iq\cdot r_1} + S_{2z}e^{iq\cdot r_2}] = \sum_q h(q)[\tfrac{1}{2}(S_{1z}+S_{2z})(e^{iq\cdot r_1}+e^{iq\cdot r_2}) + \tfrac{1}{2}(S_{1z}-S_{2z})(e^{iq\cdot r_1}-e^{iq\cdot r_2})]. \quad (1)$$

The first part has eigenvalue zero in the singlet state. The second part has nonvanishing matrix elements connecting the singlet to the $M=0$ component of each triplet excited state. As an example, we have calculated the matrix element H' between the singlet configuration $(1s)^2$ and the $M=0$ component of the triplet $(1s2p)$, using hydrogenic wave functions, and obtain

$$F \equiv (1s^2|H'|1s2p) = 2^{-\frac{1}{2}}\sum_q \int \varphi_{2p}{}^*(r_1)e^{iq\cdot r_1} \times \varphi_{1s}(r_1)d^3r_1 h(q) \qquad (2)$$

using symmetry to eliminate an integration over r_2. The remaining integral is easily performed, and we find

$$F = \sum_q 6iqa[9/4+(qa)^2]^{-3}h(q). \qquad (3)$$

The partial contribution of this process to the susceptibility $\chi(q)$ is

$$\chi(q) = \frac{72(qa)^2}{[E(2p)-E(1s)][9/4+(qa)^2]^6} \qquad (4)$$

and it is paramagnetic, i.e., the energy is lowered by the perturbation. For $qa = 0.1$, the above formula gives the value 0.005 divided by the energy difference; however, to obtain the total susceptibility, one must include contributions from higher excited states and from other closed shells. In tin, there are five closed shells of s electrons which, because of overlap at the nucleus, are capable of affecting the Knight shift. Their total effect, together with inclusion of higher excited states, may be on the order of 20 times the value given by the above calculation. For $qa = 0.3$, this value is increased yet one more order of magnitude, bringing it into the range where it could be competitive with the usual sources of Knight shift,[1] from which it is distinguished, however, by the strong dependence on wavelength or penetration depth of the magnetic field.

It is also possible to display the effect of a spatially dependent magnetic field on a correlated atom, that is, one in which electronic correlations play a nontrivial role. For this purpose it is less convenient to decompose the magnetic field into different wavelength components. Rather, we shall assume that the field exists in a substantial region of space but not in the immediate vicinity of the atom. The consequence is that, whereas the bound states of the atom are essentially unaffected by the perturbing potential, the excited state continuum is Zeeman split, and thus the virtual excitations of the electrons into the continuum, owing to their mutual interactions, will be affected by the perturbation, and the ground state will be polarized. To illustrate this we adapt an exactly soluble model of two electrons bound to an attractive well in an insulating solid. For a repulsive interaction potential U less than a calculable critical magnitude U_c the ground state is a nondegenerate singlet closed shell. The perturbation is an external field—either a magnetic field which acts on the spin of each electron, or an "exchange field" such as exists in a ferromagnet and which has the same effect as a magnetic field on the order of 10^6 Oe in lining up the electron spins—which is postulated to vanish smoothly near the atom in question so that there is no appreciable effect on phase shifts, the only effect of the perturbation being in the energy denominators. We assume that the Zeeman splitting of the continuum is ±h allowing for each spin, so that the expression for the ground-state energy becomes[3]

$$\frac{1}{U} = \frac{|f_0(0)|^4}{E-2\epsilon_b} + |f_0(0)|^2\int d\vec{k}n^2(\vec{k})\left[\frac{1}{E-\epsilon_b-\epsilon_k-h} + \frac{1}{E-\epsilon_b-\epsilon_k+h}\right] + \int d\vec{k}n^2(\vec{k})\int d\vec{k}'n^2(\vec{k}')\frac{1}{E-\epsilon_k-\epsilon_{k'}}. \qquad (5)$$

The first term, in which both particles are in the one-particle bound state, does not contribute to the polarization. The last term, representing dynamical two-particle correlations, does not contribute to the polarization because the Zeeman splittings ±h cancel when both electrons are in the continuum. Thus in this simple model the entire effect arises from terms in which a single electron is excited into the polarized continuum while the other remains bound to the atom and does not see the magnetic field. Now this is interesting because this situation is describable within the framework of the unrestricted Hartree-Fock theory,[4] which could therefore be used for more realistic atoms in cases when a convenient closed-form solution for the energy, such as (5), is not available.

Let us choose the energy zero at the bottom of the continuum ($k=0$) so that the bound-state energy ϵ_b is negative and the continuum energies ϵ_k are positive. We recall[3] that in the absence of a magnetic field, the two-particle ground-state energy, which shall be denoted E_0, lies in the range

$$2\epsilon_b \leqslant E_0 \leqslant \epsilon_b, \tag{6}$$

where it increases monotonically with U, starting from the value $2\epsilon_b$ at $U=0$ to a maximum of ϵ_b at $U=U_c$. For all values of U exceeding U_c the ground-state energy sticks to the maximum value ϵ_b (as one of the electrons has, in effect, been ionized and thus ceases to interact). So, for our study of the singlet ground state, we are restricted to the range of U less than U_c, in which range E_0 is an analytic function of the interaction strength U, denoted $E_0(U)$. Defining the susceptibility χ by

$$E(U,h)=E_0(U)-\tfrac{1}{2}\chi(U)h^2+O(h^3) \tag{7}$$

we readily find from Eq. (5)

$$\chi(U)=U^2\frac{dE_0}{dU}|f_0(0)|^2\int d\vec{k}\,n^2(\vec{k})[\epsilon_b+\epsilon_k-E_0]^{-3}. \tag{8}$$

Here, as in (5), $f_0(0)$ is the amplitude of the one-particle bound state at the site of the impurity, $n(k)/N^{1/2}$ is the same for the scattering states, and all integrals extend over the Brillouin zone appropriate to the crystal structure. The dependence on U of this formula demonstrates that electron correlations cannot be ignored when a quantitative estimate of the effect is made, although the (relatively) simple unrestricted Hartree-Fock theory may be quite adequate to take these into account.

Next, consider a ferromagnet, such as iron, in a bath of liquid helium. Regardless of whether the iron is magnetized or not (which has to do with the presence or absence of macroscopic domains), an exchange field exists within the material which is absent outside of it. To the singlet atom the discontinuity of the exchange field at the surface of the ferromagnet therefore acts as a potential well of very short range (on the order of an atomic distance) but great depth (as the effective h is on the order of an atomic energy). The hard core limits the number of atoms which can be drawn into this attractive potential, and the situation on the surface of the ferromagnet would therefore be that of a two-dimensional high-density Bose-Einstein condensate, if the potential well were deep enough to have a bound state in the direction perpendicular to the surface.

An analogous effect may explain the predilection of liquid helium for surfaces, as evidenced in the shape of the meniscus, the attraction into capillaries, etc. At the surface of many solids there exists a dipole layer associated with the work function of the material, resulting in electric fields which are otherwise absent both within and without the material. While the electric field will attract the helium because of the electric susceptibility of that atom, the potential barrier at the surface of the solid will keep the atom from penetrating, and a surface channel will be created.

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[1] Recently reviewed by Fulton Wright, Jr., Phys. Rev. 163, 420 (1967).

[2] Ref. 1, pp. 426-427.

[3] Daniel C. Mattis and Elliott H. Lieb, J. Math. Phys. 7, 2045 (1966).

[4] This theory is discussed by Arthur J. Freeman and Richard E. Watson in Magnetism, edited by G. Rado and H. Suhl (Academic Press, Inc., New York, 1965), Vol. II(A).