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Size dependence of the conduction-electron-spin-resonance *g* shift in a small sodium particle: Orthogonalized standing-wave calculations

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The conduction-electron-spin-resonance (CESR) spectra of small metallic particles are expected to exhibit very different behavior from those of bulk metals and are expected to depend on particle size. In particular, Kawabata has made a comprehensive theoretical study of the size dependence of the CESR line shape and predicts that, for very small diameters, the small-particle *g* shift contains a contribution which adds to the bulk *g* shift and which is proportional to the square of the particle diameter. In this paper we develop a formalism which enables us to reexamine the behavior of the *g* shift as a function of particle size, and we compare the predictions of this formalism with existing experimental data. The formalism we use is based upon a calculation of the *g* shift in bulk sodium by De Graaf and Overhauser, in which the conduction-electron wave functions are approximated by single orthogonalized plane waves. For a model cubic particle of sodium, we construct orthogonalized standing waves (OSW) by orthogonalizing stationary free-electron waves to the *s* and *p* core states. For clusters containing 8, 27, and 64 atoms, using both single and multiple OSW approximations, we first study the effect on the electronic-energy-level spectrum and charge density of altering the (arbitrary in our model) relation between the size of the cubic box in which the conduction electrons are confined and the number of atoms in the cluster. We then calculate in both approximations different contributions to the *g* shift and show that, in contrast with Kawabata's prediction, the major size-dependent contribution to this quantity can be written $\delta g(L)=[1-\alpha(a/L)]\,\delta g(\infty)$, where a is the lattice constant, α is a parameter of the order of unity, L is the length of an edge of the cubic box, and $\delta g(\infty)$ is the bulk *g* shift. Finally, we show that the term in the *g* shift that Kawabata calculated for small clusters is an approximation to the term in the bulk *g*-shift formalism which is usually denoted as $\delta g'''$. We calculate it in the case of a cubic sodium particle and find that it is smaller than Kawabata predicts. Our results, which are qualitatively correct for metals other than sodium, are in good agreement with recent data obtained for small magnesium particles. On the basis of this formalism, we conclude that the major size dependence of the CESR *g* shift comes from a surface effect.

I. INTRODUCTION

An important fundamental problem in the physics of condensed matter is the understanding of the evolution of various properties of materials as the sample size changes from the isolated atom to the infinite bulk; a large number of researchers[1] have thus studied the dependence of the properties of small particles on their size and shape. In addition to this fundamental interest, an increased understanding of the physics of small metal particles can have important technological applications as, for example, in the field of heterogeneous catalysis.

One usually distinguishes between two related effects which can modify the properties of small particles in comparison with bulk properties. These are surface effects and quantum size effects. A simple calculation shows that the ratio of the number of atoms at the surface of a small cluster to the number of inner atoms is of the order of $4(N)^{-1/3}$, where N is the total number of atoms in the cluster. Thus, for a 1000-atom particle, this ratio is still 0.4, an indication of the importance of surface effects for even moderately sized particles. Quantum size effects are expected to become important when the average spacing δ between adjacent energy eigenvalues of the Hamiltonian is comparable with characteristic energies such as the thermal energy or the Zeeman energy. In the free-electron picture of conduction electrons in a small metallic particle, δ is equal to $4E_F/3N$, where E_F is the Fermi energy. For example, for sodium metal, δ corresponds to a thermal energy $k_B T$ of 50 K for a 1000-atom particle. Thus, for small metallic clusters containing of the order of 1000 atoms or less, both surface effects and quantum size effects can be important.

It was first suggested by Fröhlich[2] and later by Kubo and his collaborators[3] that the electronic properties of metallic particles, such as the specific heat and magnetic susceptibility, should be strongly modified by quantum size effects. These and other workers[4,5] also suggested that the behavior of conduction-electron-spin-resonance (CESR) spectra in small metallic particles would be very different from their bulk behavior and could be used as a test of the validity of the discrete energy-level picture in a small cluster. In particular, it was qualitatively predicted[3–5] that the Elliott relaxation mechanism[6] would be quenched in a small enough particle and that the CESR lines would thus be narrow and have long relaxation times. This problem was addressed more carefully by Kawabata,[7] who also studied the size dependence of the g shift in small metal particles. He predicts that, for very small particles, the g shift contains a contribution which adds to the bulk g shift and which is proportional to L^2, where L is the average particle diameter.

To our knowledge, the only other theoretical treatments of the size dependence of the CESR g shift have been done by Myles and Buttet[8] and by Joyes and Buttet.[9] These workers assume a simple linear-chain tight-binding model of a small particle and include the effects of a "surface" by choosing the phenomenological Coulombic integrals which enter the calculation to be different for the end and inner atoms of the chain. These simple model calculations predict a size dependence of the g shift which is in disagreement with Kawabata's[7] theory and which indicates that the absolute value of the g shift should decrease with decreasing particle size.

The first successful experimental work on the CESR of very small particles was done by Taupin,[10] who observed narrow resonance lines in small platelets of Li in LiF. Since that time, different groups (see Table III) have studied CESR in small clusters of Li, Na, K, Mg, Al, Ag, Au, and Pt and have tried, with mixed success, to interpret their results on the basis of Kawabata's[7] theoretical predictions.

It is the purpose of the present paper to reexamine the evolution of the CESR g shift as a function of particle size. The formalism we use is an adaptation to small sodium particles of a calculation of the g shift in bulk sodium metal which was done by De Graaf and Overhauser[11] (referred to henceforth as DGO) using single orthogonalized plane waves (OPW) for the conduction-electron wave functions. The choice of sodium is a convenient one since it is an almost free-electron metal and since the theoretical bulk g shift, which has been extensively studied, is in good agreement with the experimental data. Furthermore, the single OPW calculation done by DGO is simple and easy to intrepret physically. While the explicit calculations presented here are for cubic sodium particles, we expect that the results should be valid for other metal particles with nearly free conduction electrons and arbitrary shape.

The remainder of this paper is organized as follows. In Sec. II we first briefly describe the single OPW wave functions used by DGO to calculate the bulk sodium g shift. We then discuss similar wave functions which we build by constructing a single orthogonalized standing wave (OSW) for a model cubic particle of sodium. Such a single OSW approximation to the conduction-electron wave functions is, however, questionable in a small metallic particle. We therefore then introduce the effect of the crystal potential, which mixes OSW of different wave vectors, and calculate the cluster wave functions in a multiple OSW approximation. We review the formalism for the bulk g shift in Sec. III and show how this quantity can be separated into different contributions. We then calculate these contributions, in both the single and multiple OSW approximations, in the case of a cubic sodium particle and show how the Kawabata[7] g shift is related to this analysis. A discussion of these g-shift calculations is given in Sec. III F. In Sec. IV we discuss some of the existing experimental results. In particular, we interpret some very recent results on small magnesium particles using the theory developed here. Finally, Sec. V contains a brief discussion and conclusions. A preliminary account of the present work was published earlier.[12]

II. CONDUCTION-ELECTRON WAVE FUNCTIONS FOR A SMALL SODIUM PARTICLE

The calculations of the electronic structure of small metal particles is a problem in itself (see, e.g., Ref. 13): There are accurate self-consistent calculations, which are unfortunately limited to a small number of atoms, and less sophisticated calculations, which can only be used in more qualitative investigations, but have the advantage of being able to describe clusters with a relatively large number of atoms.

In the present work our main objective is to describe qualitatively the evolution of the g shift as a function of particle size for sizes ranging from the free atom to the bulk metal. For this purpose we must have wave functions that include the effect of the spin-orbit coupling for clusters with an arbitrary number of atoms. We have found that these requirements can be met by adopting a theoretical picture for the electronic structure of such clusters which is based on two simplifying assumptions: (i) the validity of a simple cubic geometry for the clusters and (ii) the validity, for a finite sodium particle, of a non-self-consistent generalization of the single OPW treatment of the g shift in sodium metal which was done by DGO.[11]

It should, however, be noticed that in the DGO calculation the main contribution to the g shift is the so-called δg^P term (see Sec. III); in this calculation the "surface term" is negligible. It has, however, been shown[14] to be of the same order of magnitude as the δg^P term. We shall not estimate here this surface term, although it is clear that it could also depend on size.

A. Single OPW wave functions

Since the DGO model is the starting point of our calculation and constitutes the bulk-metal limit of our cluster model, we give here a brief account of this method.

DGO write the OPW wave function (continuous-spectrum wave function) of a conduction electron with wave vector $\vec{k}$ and spin predominantly up as

$$\psi_\uparrow(\vec{k},\vec{r})=N_\uparrow(\vec{k})\left[\frac{1}{(2\Pi)^{3/2}}\exp(i\vec{k}\cdot\vec{r})\begin{bmatrix}1\\0\end{bmatrix}-\sum_{\alpha}\beta_{\alpha\uparrow}(\vec{k})\phi_\alpha(\vec{k},\vec{r})\right]. \quad (1)$$

Here the sum is over the sodium core states, ϕ_α are the wave functions of the crystal core state derived from the atomic core state $u_\alpha(\vec{r})$, and $\beta_{\alpha\uparrow}(\vec{k})$ are the orthogonalization coefficients.

It should be noted that the spin-orbit coupling dependence of the OPW in Eq. (1) comes about solely through the orthogonalization to the spin-orbit split $2p$ core states having total angular momentum $j=\frac{1}{2}$ and $j=\frac{3}{2}$.

DGO assume a phenomenological spherical crystal potential $V(r)$, with two adjustable parameters inside the Wigner-Seitz cell. They calculate the expectation values of the Hamiltonian with spin-orbit coupling between the atomic wave functions $u_\alpha(\vec{r})$, for which they assume certain parametrized forms [see Eq. (10) of Ref. 11]. They then minimize these expectation values with respect to the parameters describing the atomic functions $u_\alpha(\vec{r})$ for each set of the parameters of the potential $V(r)$. The parameters of the core wave functions $u_\alpha(\vec{r})$ which minimize the Hamiltonian with spin-orbit coupling are given in Table II of Ref. 11.

B. Single OSW wave functions for a cubic particle of sodium

Passing now to the clusters we assume, in the spirit of the frozen core approximation, that the core states are not appreciably modified in the cluster from those in the infinite crystal. We can therefore describe the core states $u_\alpha(\vec{r})$ in the same parametrized form and with the same values of the parameters as DGO have done in their bulk sodium calculations. However, the form of the wave functions, Eq. (1), is no longer valid for the conduction electron in a cluster, owing to the presence of the propagating plane waves. In contrast with the bulk-metal case, a conduction electron in a small metallic particle feels a surface potential barrier that prevents it from spilling out of the particle.

The simplest possible way of simulating such an effect is to assume an infinite potential barrier at the surface. If we further assume that the cluster shape is a perfect cubic box of side L, we have an immediate and very simple finite size generalization of the DGO model, in which the plane waves of Eq. (1) are replaced by standing waves in a cubic box, which are orthogonalized to all core states. These wave functions are denoted as orthogonalized standing waves.

A single OSW conduction-electron wave function is then written as

$$\psi_\uparrow(\vec{\gamma},\vec{r})=A_\uparrow(\vec{\gamma})\left[s(\vec{\gamma},\vec{r})\begin{bmatrix}1\\0\end{bmatrix}-\sum_{j,\alpha}\beta_{\alpha\uparrow}(\vec{R}_j,\vec{\gamma})u_\alpha(\vec{r}-\vec{R}_j)\right], \quad (2)$$

where $s(\vec{\gamma},\vec{r})$ is a free-electron standing wave normalized to one in the volume $V=L^3$ of the cubic box. It is given by

$$s(\vec{\gamma},\vec{r})=\left[\frac{8}{V}\right]^{1/2}\sin\left[\gamma_x\left[x+\frac{L}{2}\right]\right]\sin\left[\gamma_y\left[y+\frac{L}{2}\right]\right]\sin\left[\gamma_z\left[z+\frac{L}{2}\right]\right] . \tag{3}$$

Here the origin has been taken at the center of the cube and $\vec{\gamma}=(\gamma_x,\gamma_y,\gamma_z)$ is defined by

$$\vec{\gamma}=\left[\frac{\Pi p_x}{L},\frac{\Pi p_y}{L},\frac{\Pi p_z}{L}\right] ,$$

$$p_x,p_y,p_z=1,2,3,\ldots .$$

The coefficients $\beta_{\alpha\uparrow}(\vec{R}_j,\vec{\gamma})$ in Eq. (2) are equal to

$$\beta_{\alpha\uparrow}(\vec{R}_j,\vec{\gamma})=\int_V u_\alpha^\dagger(\vec{r}-\vec{R}_j)s(\vec{\gamma},\vec{r})\begin{bmatrix}1\\0\end{bmatrix}d^3r . \tag{4}$$

The sum over lattice sites j in Eq. (2) goes over the finite number of atoms in the cluster and $A_\uparrow(\vec{\gamma})$ is a normalization coefficient approximately equal to one. We shall neglect it in what follows since it does not change the results significantly.

We establish the connection between the edge length L of the cubic box and the actual dimensions of an N-atom particle in the following way. First, we assume that the lattice parameter does not change as the sample size changes from the infinite crystal to the small cluster.[15] For further simplicity we assume that the particle has a simple cubic (sc) structure with the same average density as the body-centered cubic (bcc) structure found experimentally for bulk sodium.[16] This means that the lattice parameter a_{sc} of the sc structure is related to the lattice parameter a of the bcc structure by $a_{\text{sc}}=a/2^{1/3}$ (we use $a=7.984$ a.u. in all our calculations). The following relationship is then assumed to hold:

$$L=(N_x+\epsilon)a_{\text{sc}} , \tag{5}$$

where N_x is the number of atoms along a cube edge and ϵ is a parameter which is $\geq\frac{1}{2}$. This parameter simulates a "spill out" effect of the conduction electrons at the surface. Although the calculations can be carried out for any value of ϵ, in our single OSW approximation we only report results obtained with $\epsilon=1$. With the more refined multiple OSW calculation it will be shown below that the assumption, Eq. (5), does not significantly affect our results for the g shift.

The main advantage of our single OSW model is its great simplicity; the wave functions can be written analytically and the g factor can be easily calculated for clusters with an arbitrary number of atoms.

C. Multiple OSW wave functions for a cubic particle of sodium

As it may easily be seen, the OSW of wave vector $\vec{\gamma}$, Eq. (2), can be regarded as a particular linear combination of the OPW's, Eq. (1), having wave vector $\vec{k}$ with modulus $|\vec{k}|$ equal to $|\vec{\gamma}|$. This very special *intraband* mixing of the OPW's is the only effect of the surface barrier in the single OSW model.

This is a questionable assumption, even for cubic particles which are well described by the DGO single OPW model in the infinite crystal limit. First of all, it is known that an infinite potential barrier is a very crude approximation for describing either the surface of a metal[17] or the surface of a small particle.[15] In particular, in our cubic box model, it is important to verify that the results do not depend crucially on the distance that the electrons are allowed to spill out of the finite cube of atoms. That is, it must be verified that the choice of ϵ in Eq. (5) does not significantly affect the predictions made by this theory. Second, it should be noted that in the case of bulk metals, the crystal potential can only give rise to *interband* mixing of OPW's by coupling OPW's which differ by a reciprocal-lattice vector. These OPW's belong to states having large single OPW energy differences. Therefore, if the crystal potential is weak enough, as it is in simple metals, the single OPW approximation is a reasonable one.

In the case of a small cluster, however, the translational invariance is broken and the crystal potential couples all single OSW's having different $\vec{\gamma}$ values and which may thus be very close in energy. This corresponds to a large number of both *interband* and *intraband* mixings in the OPW picture. Therefore, the equivalent of a single OPW approximation in bulk metal is, for our model for a cluster, a multiple OPW calculation in which at least all of the possible couplings between the single OPW's belonging to the first conduction band are taken into account. This corresponds in the OSW language to a multiple OSW calculation in which all of the single OSW's having energies up to the top of the first conduction single OPW band are taken into account.

In such a multiple OSW calculation, one must solve the secular equation

$$||\langle \psi_{\vec{\gamma}s} | \mathscr{H} - E | \psi_{\vec{\gamma}'s'} \rangle|| = 0 , \tag{6}$$

where $\mathscr{H}$ is the crystal Hamiltonian and $\psi_{\vec{\gamma}s}$ denotes a single OSW of pseudo-wave-vector $\vec{\gamma}$ and spin s ($s = \uparrow$ or $\downarrow$). Owing to the close relationship between the OSW's and the OPW's, the matrix elements entering Eq. (6) can be written following the standard OPW formalism (see, e.g., Ref. 18).

For this calculation, we use a one-electron crystal Hamiltonian without spin-orbit coupling, which can thus only mix OSW's having up spin with other OSW's having up spin, and similarly for the down-spin case. Strictly speaking, the spin-orbit coupling term should also be included; however, since the spin-orbit interaction is mostly localized near the nuclei, it is a reasonable approximation to neglect it in solving Eq. (6). We assume, as in the single OSW model, that the main spin-orbit effect on the conduction-electron wave functions comes through the orthogonalization of the OSW to the $2p$ core states.

It should be noticed that once the correct cluster potential is determined, the multiple OSW approach can give essentially "exact" results for a given cluster. This is only true, however, if a sufficient number of OSW's is included in the sum and if the outermost nodes of the OSW's are sufficiently far away from the outermost atoms in the cluster.

Unfortunately, the determination of the correct cluster potential $V(\vec{r})$ is not an easy task. It is well known that in the infinite crystal case the sodium potential can be decomposed into a sum of spherical potentials $v(\vec{r})$.[19] The Fourier components of V, and therefore also those of v, are available in the literature.[20] In a small cluster, a significant fraction of the atoms are at the particle surface and these surface atoms may have potentials which are significantly different from those in the interior of the cluster. One thus expects that the decomposition into a sum of identical spherical potentials is no longer valid for a cluster. The potential $V(\vec{r})$ should, in fact, be determined via a self-consistent field approach, which would add considerable complication to our multiple OSW calculation. For simplicity we have thus taken the spherical potential v to be the same as that for bulk sodium. Even with this simplifying assumption, we find that our multiple OSW calculation gives a considerably more realistic surface potential barrier than the infinite one.

Since we want to use the same core eigenfunctions and eigenenergies as those found in the DGO paper, in our actual calculations we have chosen a potential $v(r)$ slightly modified from that given in Ref. 20. In writing down the matrix elements of the secular equation (6) it is very important that the core states be accurate representations of the true eigenstates of the crystal Hamiltonian. To this end we have used the DGO potential, in the region (internal to the Wigner-Seitz cell) where it closely resembles the potential given in Ref. 20, and we have used a form that smoothly extrapolates from the DGO potential to the potential of Ref. 20 for larger r values. In reciprocal space this consists of using the Fourier transform of the DGO potential for $q \geq \bar{q}$, with $\bar{q} = 0.68$ a.u., and in using $v(q) = A + Bq^2$, with $A = -0.939$ a.u. and $B = 0.929$ a.u. for $q < \bar{q}$.

Unfortunately, the multiple OSW calculation cannot be performed for clusters with an arbitrary number of atoms. The primary reason for this is a practical limitation on the sizes of the matrices that can be numerically diagonalized. For this reason, we have only studied sc clusters having 8, 27, and 64 atoms with the multiple OSW method.

D. Multiple OSW results: Energy levels and electronic charge densities

We have performed a detailed multiple OSW calculation for the 8-atom cluster in order to optimize our choice for the parameter ϵ [Eq. (5)]. To this end we have calculated the energies, the eigenfunctions, and the electronic charge densities for two different L values, $L = 3a_{\text{sc}}$ and $L = 4a_{\text{sc}}$. In Tables I and II, we show for both cases the energies of the highest occupied molecular orbital (denoted E_F) and of the lowest orbital (denoted E_0) as a function of the maximum energy (denoted $E_{\max}$) of the single OSW's which are included in the calculation. There is reasonably good agreement between the two calculations if we include enough OSW's; in particular, the relative occupied bandwidth with respect to the bulk metal, $\Delta E / \Delta E_{\infty}$, converges towards the same value, ~ 0.59. The electronic charge densities obtained with the two L values are shown in Fig. 1. They are very similar and they each tail off at distances x smaller than the infinite potential barrier for the smallest box, i.e., for x / a_{sc} values smaller than 1.5.

TABLE I. Orbital energies and g-shift values for an 8-atom cluster of sodium in the multiple OSW approximation for $L=3a_{\mathrm{sc}}$. $E_{\max}$ is the maximum energy of the single OSW which are mixed into the multiple OSW wave function, E_F and E_0 are, respectively, the highest and lowest occupied molecular orbitals, $\Delta E/E_\infty$ is the relative bandwidth, and δg_d^p and δg_{od}^p are the calculated diagonal and off-diagonal components of the g-shift contribution δg^p.

$E_{\max}$ (eV)	E_F (eV)	E_0 (eV)	$\Delta E/E_\infty$	δg_d^p ($\times 10^{-4}$)	δg_{od}^p ($\times 10^{-4}$)	δg^p ($\times 10^{-4}$)
3.24	−3.477	−5.996	0.74	−0.777	−0.000	−0.777
5.84	−3.833	−6.729	0.85	−0.932	−0.444	−1.38
7.32	−4.748	−6.816	0.61	−1.01	−0.136	−1.15
8.44	−4.766	−6.816	0.60	−1.02	−0.147	−1.17
9.18	−4.766	−6.816	0.60	−1.02	−0.147	−1.17
11.40	−4.972	−6.957	0.58	−1.06	−0.426	−1.49
14.37	−4.986	−6.980	0.59	−1.07	−0.482	−1.55

On the same graph we also show the electronic charge density (dot-dashed curve) obtained for the same size cluster with a single OSW. Although the overall shape of this curve is similar to the multiple OSW results, there are marked differences which show the importance of the mixing of single OSW's by the crystal potential.

These calculations show that the choice $L=(N_x+1)a_{\mathrm{ac}}$, corresponding to $\epsilon=1$, is sufficient to avoid a significant influence of the box edge on the surface tail of the charge density. Furthermore, from the results shown in Table I, it can be seen that an $E_{\max}$ value of 10 eV is necessary to obtain a reasonable convergence for the energies of the occupied states. All of the subsequent calculations on the 27- and 64-atom clusters were done with this choice for L and $E_{\max}$. The electronic charge densities at the surface of the 27- and 64-atom clusters behave essentially as they do in the 8-atom cluster. The calculated orbital energies for the sodium clusters studied within the multiple OSW scheme are reported in Fig. 2. The high-level degeneracy is due to the assumed perfect cubic shape of the particles. It should also be noted that, for the 27-atom cluster, the occupied bandwidth has already reached its infinite crystal limit. This behavior is in agreement with self-consistent calculations done on the basis of the $X\alpha$ method. For example, Salahub and Messmer[21] obtain 99% of the experimental bandwidth for 43-atom aluminum clusters using this method. Finally, it should be pointed out that the surface tails of our calculated charge densities are in qualitative agreement with self-consistent calculations for a semi-infinite jellium surface[17] and with variational calculations for a spherical jellium model of simple metal clusters.[15]

III. CALCULATION OF THE g SHIFT

The basic theory of the g shift in bulk materials is complicated. The main reason for this is that even a small magnetic field has a large effect on the conduction-electron wave functions, which extend to infinity throughout the bulk crystal. Following the work of earlier researchers, Yafet[22] has developed a detailed formalism for the calculation

TABLE II. Orbital energies and g-shift values for an 8-atom cluster in the multiple OSW approximation for $L=4a_{\mathrm{sc}}$. All symbols are defined as in Table I.

$E_{\max}$ (eV)	E_F (eV)	E_0 (eV)	$\Delta E/E_\infty$	δg_d^p ($\times 10^{-4}$)	δg_{od}^p ($\times 10^{-4}$)	δg^p ($\times 10^{-4}$)
3.24	−2.134	−6.131	1.18	−0.429	−0.267	−0.70
5.12	−3.699	−6.712	0.89	−0.352	0.375	−0.73
7.42	−4.551	−6.791	0.66	−0.416	−0.923	−1.34
8.04	−4.950	−6.791	0.60	−0.434	−0.781	−1.22
8.88	−4.759	−6.791	0.60	−0.438	−0.878	−1.32
10.75	−4.893	−6.866	0.58	−0.448	−1.01	−1.45

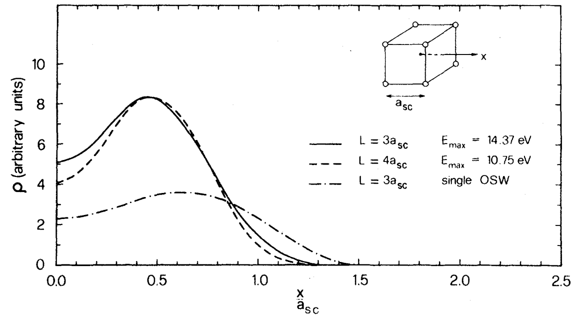

FIG. 1. Electronic charge density for an 8-atom cluster of sodium in the OSW approximation. The solid curve and the dashed curve correspond to multiple OSW calculations with, respectively, $L=3a_{\text{sc}}$ and $L=4a_{\text{sc}}$. The dot-dashed curve is the electronic charge density in the single OSW approximation with $L=3a_{\text{sc}}$. $E_{\max}$ is the maximum energy of the single OSW which are mixed into the multiple OSW wave function.

of the g shift in an infinite crystal. On the other hand, the calculation of the g shift in molecules is easier than that for a bulk crystal; it has been done using perturbation theory in the spin-orbit coupling.[23] It can be proven that the difficulties associated with gauge transformations of the vector potential which are encountered in the infinite crystal g-shift formalism can be solved in the molecular formalism if both the first- and second-order terms in the perturbation series in the spin-orbit coupling are taken into account.[23,24] There is, to our knowledge, no general theory of the g shift which unifies the infinite crystal and molecular g-shift formalisms. Such a theory would be the ideal formalism with which to study the dependence of the g shift on particle size for a small cluster. Since a general theory does not exist, we shall in the present work use the bulk crystal formalism and we shall keep only the terms which converge towards the bulk g shift as the size of the cluster increases [see Eq. (19)].

A. Bulk g-shift formalism

Here we shall use the bulk g-shift formalism developed by De Graaf and Overhauser[25] and later modified by Moore.[26] This formalism is based upon the fact that the Zeeman splitting $g\mu_B H$ is linear in the external magnetic field. Here μ_B is the Bohr magneton, H is the magnetic field, and g is the g factor of interest. Thus, in order to calculate the g factor, one needs only to consider terms in the perturbing Zeeman Hamiltonian which are linear in the external magnetic field. Furthermore, first-order perturbation theory is sufficient and in order to obtain the g factor one calculates the difference in the expectation value of this perturbation between the conduction-electron wave functions which have spin predominantly up and that between states with spin predominantly down. There are, however, several difficulties, one of which is the requirement that any physical theory be gauge invariant. The one-particle Dirac equation, which is used as a starting point for the g-shift formalism, satisfies this requirement. It is clear that the reduction from the Dirac equation to the Pauli equation for the two-component spinor must retain this gauge invariance. De Graaf and Overhauser[25] show that if one chooses to describe the conduction electron by a wave packet in the standard form

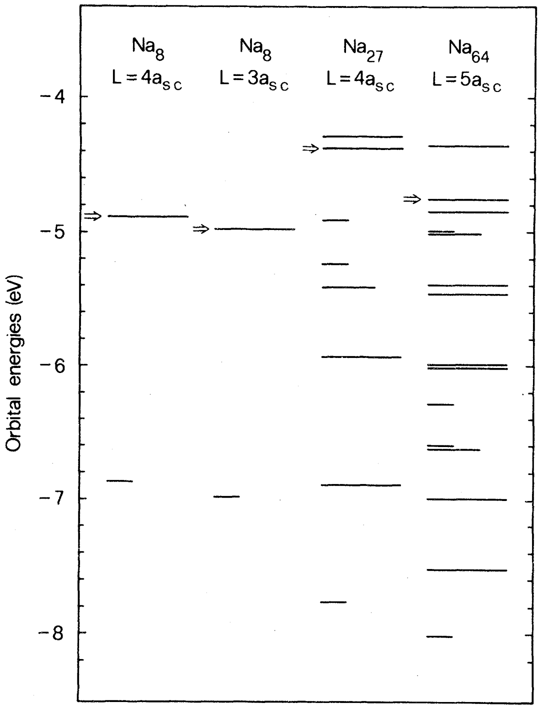

FIG. 2. Orbital energies obtained for a sodium particle within the multiple OSW approximation. The maximum energies of the single OSW wave functions which are mixed into the multiple OSW wave functions are, respectively, 10.75, 14.37, 13.06, and 9.52 eV for the 8-atom ($L=4a_{\text{sc}}$), 8-atom ($L=3a_{\text{sc}}$), 27-atom ($L=4a_{\text{sc}}$), and 64-atom ($L=5a_{\text{sc}}$) clusters. The bandwidth of the infinite sc crystal is equal to 3.41 eV. The lengths of the horizontal lines are proportional to the orbital degeneracy (equal to 1, 2, or 3) of the state represented. The arrow indicates the highest occupied energy level.

$$\Psi_\uparrow(\vec{k},\vec{r}) = \int f(\vec{k}-\vec{k}\,')\psi_\uparrow(\vec{k}\,',\vec{r})\,d^3k' \,, \tag{7}$$

where the integral is over all values of $\vec{k}\,'$ and

$f(\vec{k}-\vec{k}\,')$ is nonzero only in a small volume of $\vec{k}\,'$ space centered at $\vec{k}$, then the Jones and Zener gauge must be used. Moore[26] points out that since this choice of gauge produces a time-dependent Hamiltonian an extra term must be added to the Hamiltonian to enable the average energy to be calculated in the usual way. The choice of the wave-packet representation for the wave functions has the advantage of solving the difficulties with the position operator $\vec{r}$, which is not a bounded operator in an infinite crystal. DGO and Moore (referred to collectively in what follows as DGOM) thus calculate the g factor as

$$\mu_B H g(\vec{k}) = \langle \Psi_\uparrow(\vec{k},\vec{r}) \,|\, \mathscr{H}_{g\uparrow} \,|\, \Psi_\uparrow(\vec{k},\vec{r})\rangle - \langle \Psi_\downarrow(\vec{k},\vec{r}) \,|\, \mathscr{H}_{g\downarrow} \,|\, \Psi_\downarrow(\vec{k},\vec{r})\rangle \;, \tag{8}$$

where $\mathscr{H}_{g\uparrow}$ and $\mathscr{H}_{g\downarrow}$ are the parts of the perturbing Hamiltonian which are linear in the magnetic field for predominantly spin-up and spin-down states, respectively.

DGOM have shown that the Hamiltonians $\mathscr{H}_{g\uparrow}$ and $\mathscr{H}_{g\downarrow}$ have the form

$$\mathscr{H}_g = \frac{\mu_B H}{\hbar}[(x-\langle x\rangle)\Pi_y - (y-\langle y\rangle)\Pi_x] + \mu_B H \sigma_z \left[1 - \frac{p^2}{2m^2c^2}\right] , \tag{9}$$

where σ_z is a Pauli spin matrix, and $\langle x\rangle$ and $\langle y\rangle$ are the expectation values of x and y with respect to the wave packets $\Psi_\uparrow(\vec{k},\vec{r})$ for $\mathscr{H}_{g\uparrow}$ and $\Psi_\downarrow(\vec{k},\vec{r})$ for $\mathscr{H}_{g\downarrow}$. The operator $\vec{\Pi}$ in Eq. (9) is given by

$$\vec{\Pi} = \vec{p} + \frac{e\hbar}{4mc^2}\vec{\sigma}\times\vec{\nabla}V \;,$$

where $\vec{p}$ is the usual free-electron momentum operator $-i\hbar\vec{\nabla}$ and V is the crystal potential.

Singh *et al.*[27] have more recently calculated the g factor for iron and nickel using tight-binding wave functions. They have shown that if one chooses the symmetric gauge, one will arrive at the same g-factor formalism as DGOM.

Beginning with Eq. (8), DGOM have shown that the bulk g shift $\delta g(\vec{k}) = g(\vec{k}) - g_e$ can be written

$$\delta g(\vec{k}) = \delta g^p(\vec{k}) - \frac{2i}{\hbar}\int \left[\frac{\partial\psi_\uparrow^\dagger}{\partial k_x}\Pi_y\psi_\uparrow - \frac{\partial\psi_\uparrow^\dagger}{\partial k_y}\Pi_x\Psi_\uparrow\right] d^3r - 2\left[\left\{i\frac{\partial}{\partial k_x}\right\}\{\Pi_y\} - \left\{i\frac{\partial}{\partial k_y}\right\}\{\Pi_x\}\right] - 2(\{x\}\{\Pi_y\} - \{y\}\{\Pi_x\}) + \delta g'(\vec{k}) + \delta g''(\vec{k}) + \delta g'''(\vec{k}) \;, \tag{10}$$

where, for an arbitrary operator O, we have defined

$$\{O\} = \frac{(2\Pi)^3}{\Omega}\int_\Omega \psi_\uparrow^\dagger(\vec{k},\vec{r})\,O\,\psi_\uparrow(\vec{k},\vec{r})\,d^3r \;,$$

and $\psi_\uparrow(\vec{k},\vec{r})$ is a continuous-spectrum Bloch function normalized over all space and evaluated at a wave vector $\vec{k}$ on the Fermi surface. The first and second terms of $\delta g(\vec{k})$ come from the terms corresponding to the angular-momentum operator $\vec{r}\times\vec{p}$ in the Hamiltonian $\mathscr{H}_{g\uparrow}$ and $\mathscr{H}_{g\downarrow}$. The first term has the form

$$\delta g^p(\vec{k}) = \frac{2}{\hbar}\{x p_y - y p_x\} \;. \tag{11}$$

The third and fourth terms in Eq. (10) come from terms which correspond to $-\langle\vec{r}\rangle\times\vec{\Pi}$. The term which is denoted as $\delta g'(\vec{k})$ comes from the spin-orbit-dependent contribution of the operator $\vec{\Pi}$ to the $\vec{r}\times\vec{\Pi}$ term. It thus already depends upon the spin-orbit coupling and can be evaluated with wave functions which do not include the spin-orbit contribution. DGO have shown that it has the form[25]

$$\delta g'(\vec{k}) = \frac{(2\Pi)^3}{\Omega}\frac{1}{2mc^2}\int_\Omega \psi^\dagger(\vec{k},\vec{r})\left[x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y}\right]\psi(\vec{k},\vec{r})\,d^3r \;, \tag{12}$$

where $\psi(\vec{k},\vec{r})$ is a conduction-electron wave function without the effects of the spin-orbit interaction included and V is the crystal potential. The term denoted as $\delta g''(\vec{k})$ in Eq. (10) is a relativistic contribution which comes from the correction to the term $\mu_B H\sigma_z$ in Eq. (9). It has the form

$$\delta g''(\vec{k}) = \frac{-(2\Pi)^3}{\Omega}\frac{1}{m^2c^2}\int_\Omega \psi^\dagger(\vec{k},\vec{r})(\vec{p})^2\psi(\vec{k},\vec{r})\,d^3r \;. \tag{13}$$

For the case of an isolated atom, DGO have shown that the g shift reduces to $\delta g = \delta g' + \delta g''$.

The term denoted as $\delta g'''(k)$ in Eq. (10) has the form

$$\delta g'''(\vec{k}) = \frac{(2\Pi)^3}{\Omega} 2\int_\Omega \psi_\uparrow^\dagger(\vec{k},\vec{r})(\sigma_z - 1)\psi_\uparrow(\vec{k},\vec{r})d^3r . \tag{14}$$

DGO[25] have shown (see also Yafet[22]) that the second, third, and fourth terms of the g shift in Eq. (10) can be transformed into surface integrals over the boundary of a Wigner-Seitz cell. If the spin-orbit-dependent parts of the conduction-electron wave functions (i.e., the core wave functions in our OSW model) are vanishingly small at the cell boundary, these terms will therefore be very small. This is the approximation that DGO used in their OPW g-shift calculation for sodium. In that calculation, they have shown that the main contribution to the g shift comes from the term denoted as $\delta g^p(\vec{k})$.

In order to make a comparison between the calculated g shift and those measured in experiment, one must average $\delta g(\vec{k})$ over all wave vectors on the Fermi surface. Such averaging takes into account the (in a bulk metal) short scattering time of the conduction electrons at the Fermi level. In this regard, it is worth noting that the frequency-dependent CESR linewidth in aluminum has been interpreted as due to the imperfect averaging of $\delta g(\vec{k})$.[28]

In a small particle, where the electronic energy levels are discrete, it is expected that the conduction electrons are not easily scattered from one state to another; the scattering time at the Fermi surface is thus long and each particle in a sample has a nonaveraged g value. If consideration is given to the fact that the various particles in a sample have different (irregular) shapes and sizes, it is thus expected that the measured g values will be spread in a distribution centered about an average g value. The CESR linewidth of an ensemble of particles should thus depend linearly on the magnetic field, if the distribution of g values is the main source of broadening.

B. Bulk sodium g shift

As was discussed earlier, DGO[11] have shown that the main contribution to the g shift in bulk sodium is $\delta g^p(\vec{k})$, given by Eq. (11). Using that equation and their OPW wave functions, we obtain for this quantity in bulk sodium metal

$$\delta g^p(k_F) = \frac{48\Pi}{\Omega} J_p(k_F) J_\Delta(k_F) \frac{\langle k_{xF}^2 + k_{yF}^2 \rangle}{k_F^2} , \tag{15}$$

where the angular brackets denote the average over all Fermi wave vectors $\vec{k}_F$, k_{xF} and k_{yF} are the x and y components of $\vec{k}_F$, and we have defined the functions

$$J_p(k_F) = \tfrac{1}{3}[J_{1/2}(k_F) + 2J_{3/2}(k_F)] \tag{16a}$$

and

$$J_\Delta(k_F) = \tfrac{1}{3}[J_{1/2}(k_F) - J_{3/2}(k_F)] , \tag{16b}$$

in which

$$J_\alpha(k_F) = \int_0^\infty R_\alpha(r) j_1(k_F r) r^2 dr . \tag{17}$$

Here $R_\alpha(r)$ is the radial part of the core wave functions $u_\alpha(\vec{r})$ and $j_1(k_F r)$ is a spherical Bessel function. The expression for $\delta g^p(k_F)$, Eq. (15), is valid to all orders in the Fermi wave vector $\vec{k}_F$, in contrast with the results obtained by DGO, who calculated this quantity to only second order in $\vec{k}_F$. We have numerically evaluated this contribution to the g shift of bulk sodium, the result of this calculation is $\delta g^p = -2.82 \times 10^{-4}$.

Using these same OPW wave functions, we have also calculated the contribution $\delta g''(k_F)$ [Eq. (13)] for bulk sodium to all orders in k_F. Numerically, we find $\delta g'' = -0.50 \times 10^{-4}$. Also using these wave functions, DGO have calculated the contribution to the bulk sodium g shift denoted as $\delta g'(k_F)$ and given by Eq. (12). They find $\delta g' = 0.11 \times 10^{-4}$. As is discussed in subsection D below, the contribution $\delta g'''(k_F)$, given by Eq. (14), is very small for an infinite crystal, and makes a negligible contribution to the bulk sodium g shift.

Taking into account the above results, we find for the total g shift in bulk sodium $\delta g = \delta g^p + \delta g'' + \delta g' = -3.21 \times 10^{-4}$. This value is not in good agreement with the bulk experimental g shift for sodium, which is equal to $\delta g = (-8 \pm 2) \times 10^{-4}$.[29] Moore and Liu[14,30] have calculated the g shift in sodium using a spherical wave expansion for the wave functions. They have shown that the surface terms on the boundary of the Wigner-Seitz cell cannot be neglected as DGO have done. In their calculation, the sum of these terms is equal to -2.87×10^{-4}. The term δg^p calculated by DGO is thus an important contribution to the g shift in sodium, although not the only one. In the present paper, we shall keep the DGO model and neglect these surface terms, which would be very difficult to evaluate in a small cluster.

C. Size dependence of the δg^p term; single and multiple OSW approximations

In a small metallic particle, one need not write the conduction-electron wave functions as wave packets, since the position operator $\vec{r}$ is bounded in this case and the electron energy levels are discrete. We shall thus calculate $\delta g(\vec{k})$ for a small particle of sodium using in Eq. (8) the OSW wave function corresponding to the highest occupied energy level. The operator $\langle\vec{r}\rangle \wedge \vec{\Pi}$ in the Hamiltonian $\mathscr{H}_g$ [Eq. (9)] will be neglected here, since it is closely related to the choice of a wave-packet description for the conduction-electron wave functions. Furthermore it can be shown that it gives a negligible contribution in the OSW approximation; physically this is due to the fact that the average value of the momentum $\vec{p}$ is very small in this approximation.

In the single OSW approximation, we thus have

$$\delta g^p(\gamma_F)=\frac{1}{\hbar}\int_V d^3r\,\psi_\uparrow^\dagger(\vec{\gamma}_F,\vec{r})(xp_y-yp_x)\psi_\uparrow(\vec{\gamma}_F,\vec{r})d^3r-\frac{1}{\hbar}\int_V d^3r\,\psi_\downarrow^\dagger(\vec{\gamma}_F,r)(xp_y-yp_x)\psi_\downarrow(\vec{\gamma}_F,\vec{r})d^3r\ , \quad (18)$$

where $\psi_\uparrow(\vec{\gamma}_F,\vec{r})$ is the single OSW wave function given by Eq. (2) and $\vec{\gamma}_F$ is the $\vec{\gamma}$ value of the highest occupied single OSW. Such a calculation assumes, however, that the wave functions are orbitally nondegenerate. This is in general not true for cubic particles, where the orbital degeneracy of levels is high. In a real cluster, whose shapes are irregular, one expects a lifting of this orbital degeneracy. We thus shall make the calculation as if the levels are nondegenerate and then take an average of $\delta g^P(\gamma_F)$ over the different degenerate states. Upon evaluating $\delta g^P(\gamma_F)$ one finds that there are three different kinds of matrix elements which enter the calculation. We denote these as *s-s*, *s-c*, and *c-c*, where *s-s* corresponds to matrix elements of the standing wave part of $\psi_\uparrow^\dagger(\vec{\gamma}_F,\vec{r})$ with the standing wave part of $\psi_\uparrow(\vec{\gamma}_F,\vec{r})$, *s-c* corresponds to matrix elements of the standing wave part of $\psi_\uparrow^\dagger(\vec{\gamma}_F,\vec{r})$ with the core part of $\psi_\uparrow(\vec{\gamma}_F,\vec{r})$, and *c-c* corresponds to core-core matrix elements. The *s-s* matrix elements are zero and both the *s-c* and *c-c* elements can be decomposed into two terms. For the case of *c-c* matrix elements we obtain, for example,

$$\sum_{\alpha,\alpha',j}\beta_{\alpha\uparrow}^*(\vec{R}_j,\vec{\gamma}_F)\beta_{\alpha'\uparrow}(\vec{R}_j,\vec{\gamma}_F)\left[\int u_\alpha^\dagger(\vec{r}-\vec{R}_j)[(\vec{r}-\vec{R}_j)\times\vec{p}]u_{\alpha'}(\vec{r}-\vec{R}_j)+\vec{R}_j\times\int u_\alpha^\dagger(\vec{r}-\vec{R}_j)\vec{p}u_{\alpha'}(\vec{r}-\vec{R}_j)\right], \quad (19)$$

where, in the first term, the angular-momentum operator is centered on the corresponding core wave function. As the cluster size decreases, the sums of the first terms calculated for the *s-c* and *c-c* contributions tend towards their bulk values. We have found that, even for very large clusters, the second terms do not go to zero and that there is no easy way of seeing how they could cancel with other terms or be related to known bulk contributions. This is a basic difficulty which can be traced back to the wave-packet description in the bulk *g*-shift formalism, which introduces additional terms in the *g* shift. We have circumvented this difficulty by keeping only those terms which reduce to the bulk value in the limit of large clusters.

For simplicity, here we only show explicit single OSW results for $\delta g^p(\gamma_F)$ in the special case where the edge length L of the conduction-electron box is equal to $(N_x+1)a_{\rm sc}$. Clearly, results for other choices of the relationship between L and N_x are also easily obtained. In this case, the results of evaluating Eq. (18) are

$$\delta g^p(\gamma_F)=\frac{48\Pi}{\Omega}\left[1-\frac{2a_{\rm sc}}{L}\right]J_p(\gamma_F)J_\Delta(\gamma_F)\times\frac{\langle\gamma_{xF}^2+\gamma_{yF}^2\rangle}{\gamma_F^2}\ , \quad (20)$$

where γ_{xF} and γ_{yF} are the x and y components of $\vec{\gamma}_F$, the angular brackets denote an average over the degenerate states of the highest occupied energy level, and J_p,J_Δ are defined in Eq. (16). The dominant size dependence of δg^p lies in the factor $(1-2a_{\rm sc}/L)$; the value for γ_F has also a size dependence, but it does not significantly modify the general size-dependent behavior of δg^p. In Ref. 12 we have given explicit results for $\delta g^p(\gamma_F)$ for the case of a bcc crystal lattice with the choice of $L=(N_x'+1)a/2$, where N_x' is the number of atoms along the bcc cube edge and a is the bcc lattice parameter. The result shown in Eq. (20) is the same as that given in Ref. 12 if one replaces $2a_{\rm sc}$ by a. We have found that the precise multiplicative factor in front of the $a_{\rm sc}/L$ size-dependent correction to $\delta g^p(\gamma_F)$ depends on the relationship one chooses between the length L and the number of edge atoms N_x. Given a particular choice of this relationship, this multiplicative factor can be obtained easily. We thus find that the primary size dependence of the contribution $\delta g^p(\gamma_F)$ may be written in the single OSW approximation as

$$\delta g^p(\gamma_F) \simeq \left[1-\alpha\frac{a}{L}\right]\delta g^p(\infty)\,, \tag{21}$$

where $\delta g^p(\infty)$ is the value obtained for this term in the bulk [Eq. (15)], α is a positive parameter of order one which depends upon the relationship between L and N_x, and the size dependence of γ_F has been neglected.

As discussed above, it is important to compare the general behavior predicted by Eq. (21) with a multiple OSW calculation. The calculation of δg^p in this approximation is similar to that discussed above for the single OSW approximation. Using the multiple OSW wave functions and beginning with Eq. (18), we have calculated $\delta g^p(n_F)$, where n_F labels the highest occupied multiple OSW wave function. In this case, δg^p can be decomposed into the sum of diagonal terms ($\vec{\gamma}=\vec{\gamma}\,'$) and off-diagonal terms ($\vec{\gamma}\neq\vec{\gamma}\,'$). In Tables I and II we show, for two different 8-atom clusters, corresponding to $L=3a_{\rm sc}$ and $L=4a_{\rm sc}$, the dependence of the diagonal (δg_d^p) and off-diagonal (δg_{od}^p) terms in $\delta g^p(n_F)$ on the maximum energy ($E_{\max}$) of the single OSW which are mixed into the multiple OSW functions. It should be noted that, although the diagonal and off-diagonal parts of this contribution to the g shift are different for 8-atom clusters with $L=3a_{\rm sc}$ and $L=4a_{\rm sc}$, the total δg^p converges towards approximately the same value in both cases as $E_{\max}$ increases.

We show in Fig. 3 the results obtained for δg^p as a function of both L and N_x. The triangles denote the results obtained using the single OSW approximation [Eq. (20)], where the size dependence of γ_F is also included; the circles denote the results obtained using a multiple OSW approximation, and the solid line indicates the single OSW results given by Eq. (21), where the size dependence of γ_F is neglected. Since the off-diagonal elements of δg^p are only slowly convergent as $E_{\max}$ increases (see Table I and II), we have introduced error bars into the multiple OSW results. The reason for the large error bar in the case of the 64-atom clusters is that, although 238 single OSW up to $E_{\max}=9.52$ eV were used, we were at the limit of our computational capability and were not able to quite reach convergence.

From these results we can conclude that the trend obtained for δg^p in the single OSW approximation is not significantly modified by the introduction of a multiple OSW model. Equation (21) thus gives the correct trend for the evolution of δg^p as a function of particle size, despite the simplicity of the wave functions which were used to calculate it.

D. Size dependence of the term $\delta g''$; the atomic g shift

In the limit of a single atom, the g shift reduces to the sum of the two terms $\delta g'$ and $\delta g''$, defined in Eqs. (12) and (13).[25] The $\delta g'$ term is small for sodium (DGO obtain 0.11×10^{-4} for bulk sodium); thus we have not estimated its size dependence. However, we have calculated the size dependence of $\delta g''$ in the single OSW model. In the approximation where $\vec{\gamma}_F$ is approximated by its infinite crystal counterpart $\vec{k}_F$, we find that $\delta g''$ may be written in the form

$$\delta g''(\gamma_F) \simeq \delta g''(a) + [\delta g''(\infty)-\delta g''(a)]\left[1-\frac{a}{L}\right]\,, \tag{22}$$

where $\delta g''(a)$ is the value of $\delta g''$ obtained when there is only one atom left in the cubic box,

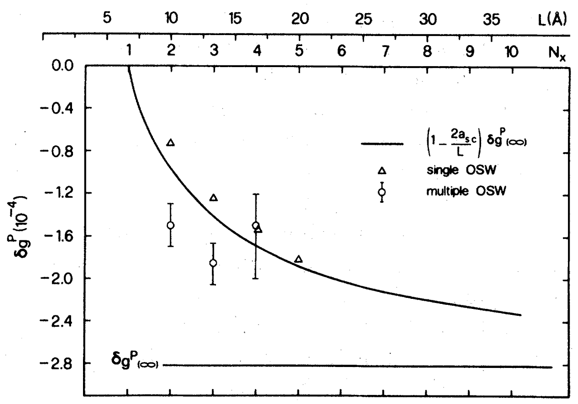

FIG. 3. δg^p for a sodium particle as a function of the number N_x of atoms along a cube edge in the single (triangles) and multiple (circles) OSW approximations. The length of an edge of the conduction-electron box was chosen equal to $L=(N+1)a_{\rm sc}$ where $a_{\rm sc}=6.334$ a.u. The solid curve represents the function $(1-2a_{\rm sc}/L)\delta g^p(\infty)$. The results obtained in the single OSW approximation using the exact result, Eq. (20), or the approximate one, Eq. (21), are almost indistinguishable on the scale of the figure for $N_x>5$.

$\delta g''(\infty)$ is its bulk value, and we have assumed a bcc lattice with $L=(N'_x+1)a/2$. Numerically we find $\delta g''(a)=-0.17\times10^{-4}$ and $\delta g''(\infty)=-0.50\times10^{-4}$. Using the relation $\delta g'(a)=-\frac{1}{3}\delta g''(a)$ established in Ref. 25, and using $\delta g(a)=\delta g'(a)+\delta g''(a)$, we obtain an atomic g shift in the single OSW approximation which has the value $\delta g(a)=-0.11\times10^{-4}$. The experimental value is equal to -0.25×10^{-4}, not in very good agreement with our theoretical prediction. However, this is not too surprising since the present theory was not intended for use in atomic g-shift problems and the OSW wave functions are certainly not expected to be valid for a single atom.

E. Size dependence of the $\delta g'''$ term; the Kawabata g shift

The term in the g shift denoted as $\delta g'''$, given by Eq. (14), is very small in bulk metal but could become larger in a small cluster. In the Appendix we show that, if this quantity is calculated in a second-order perturbation theory in the spin-orbit interaction, one obtains the g-shift contribution that Kawabata[7] has calculated for a small metallic particle. Since Kawabata's term has been used as the basis for the interpretation of data in many different experiments (see, e.g., Table III), it is important to closely study this contribution on the basis of the present model. First, however, it is worthwhile to briefly review Kawabata's[7] theory of the small-particle g shift.

Kawabata chooses a semiclassical model and calculates the CESR g shift and linewidth using a linear response formalism along with second-order perturbation theory in the spin-orbit interaction. The conduction-electron wave functions in his model are described by size-independent wave packets; the size dependences he obtains for the g-shift and spin-lattice relaxation time in CESR come from assuming that the electrons scatter diffusively at the surface of a spherical cluster and not, as in our model, from any dependence of the wave functions on particle size.

Kawabata[7] introduces a "quantum limit," defined for a particle of mean diameter L by $\hbar\omega_z \ll \delta(L)$ and $\hbar/\tau \ll \delta(L)$, where $\hbar\omega_z$ is the Zeeman energy, $\delta(L)$ is the average spacing between the discrete electronic energy levels at the Fermi surface, and τ is the spin-lattice relaxation time of the conduction electrons. In this limit he obtains a g shift for state n at the Fermi surface of the form

$$\delta g_K(L)=\delta g(\infty)-\frac{2\hbar}{\Pi}\frac{\delta(L)}{\tau}\sum_{m\neq n}\left[\frac{1}{\epsilon_{mn}}\right]^2, \tag{23}$$

where the subscript K means that the g shift is calculated in Kawabata's model, ϵ_{mn} is the energy difference between the one-electron states n and m at the Fermi energy, and $\delta g(\infty)$ is the bulk g shift. The spin-lattice relaxation time τ is defined by

$$\frac{1}{\tau}=\frac{2\Pi}{\hbar}\frac{1}{\delta(L)}\langle|\langle\psi_{n\uparrow}|\mathscr{H}_{\rm so}|\psi_{m\downarrow}\rangle|^2\rangle\ , \tag{24}$$

where $\mathscr{H}_{\rm so}$ is the spin-orbit interaction, $\psi_{n\uparrow}$ is the predominately spin-up eigenfunction corresponding to state n at the Fermi energy, $\psi_{m\downarrow}$ is the predominately spin-down eigenfunction corresponding to state $m\,(\neq n)$ near the Fermi energy, and the outer angular brackets denote an average over all such states. Kawabata[7] then calculates the average matrix elements of the spin-orbit interaction which occur in Eq. (24) and shows that τ in a small cluster is still given by the Elliott relation,[6]

$$\frac{1}{\tau}\cong\frac{[\delta g(\infty)]^2}{L/v_F}\ , \tag{25}$$

where v_F is the velocity of the conduction electrons at the Fermi surface.

Upon replacing the τ which occurs in Eq. (23) by its definition given in Eq. (24), we obtain

$$\delta g_K(L)=\delta g(\infty)-4\sum_{m\neq n}\frac{\langle|\langle\psi_{n\uparrow}|\mathscr{H}_{\rm so}|\psi_{m\downarrow}\rangle^2|\rangle}{(\epsilon_{mn})^2}\ . \tag{26}$$

In the Appendix we show that if one begins with the exact expression, Eq. (14), for the g-shift contribution $\delta g'''$, uses wave functions which (following Kawabata) are eigenfunctions of the crystal Hamiltonian plus the Zeeman interaction, treats the spin-orbit interaction as a perturbation to second order, and averages over the Fermi surface, one obtains a result for $\delta g'''$ equal to the second term of Eq. (26). We shall in what follows denote it $\delta g_2'''(L)$, where the subscript 2 shows that the expression is valid to second order in perturbation theory. It is also easy to show [Eq. (24) and the Appendix] that the conditions for validity of the perturbation theory correspond to Kawabata's quantum-limit condition $\hbar/\tau \ll \delta$.

The results discussed in Sec. III D show that, in contrast with Kawabata's predictions, *the size-dependent g shift given by Eq. (26) does not*

TABLE III. Experimental g-shift values for atoms, bulk metals, and small metallic particles.

Metal	Matrix	Average diameter (Å)	g shift[a]	Reference
Li		atom	-1×10^{-5}	
		bulk	$(-6.1\pm0.2)\times10^{-5}$	
	LiF	$3\times30\times30$[b]	$<10^{-4}$	10
	xenon	20→1000	$<10^{-4}$	32
	LiH	~50		33
Na		atom	-1×10^{-5}	
	argon	atom	$-2,6\times10^{-3}\rightarrow1.0\times10^{-3}$[c]	
		bulk	$(-8\pm2)\times10^{-4}$	
	argon	Na_3	$(-1.2\pm1.2)\times10^{-3}$	34
	NaN_3	20→1000	bulk value	35
	NaN_3	20→1000	bulk value	36
K		atom	-1×10^{-5}	
	argon	atom	$-3\times10^{-3}\rightarrow-1.4\times10^{-3}$[c]	37
		bulk	$(-2.6\pm0.1)\times10^{-3}$	
	argon	K_3	$(-3.8\pm0.5)\times10^{-3}$	37
	KN_3	(14)[d]	$(-4.5\pm0.5)\times10^{-3}$	38
	KCl	(10−20)[d]	$(-2.5\pm0.5)\times10^{-3}$	39
Mg		bulk	$(8\pm2)\times10^{-2}$[e]	
			$(0\pm1)\times10^{-2}$	
	xenon	12	$(0.7\pm0.3)\times10^{-2}$	40
	xenon	17	$(1.9\pm0.3)\times10^{-2}$	
	xenon	22	$(2.7\pm0.3)\times10^{-2}$	
	xenon	29	$(3.2\pm0.3)\times10^{-2}$	
Al	CO_2 or C_6H_6	bulk	$(-5\pm1)\times10^{-3}$	
		10→200	$0.1\rightarrow1.3\times10^{-2}$	41
Ag		atom	-8×10^{-5}	
		bulk	$(-1.9\pm0.1)\times10^{-2}$	
	KCl	50→300	$(3.2\pm0.1)\times10^{-3}$	42
	CO_2, C_6H_6 $C_{18}H_{38}$	~20	$(5.2\pm7.7)\times10^{-3}$[f]	43
Au		atom	1.8×10^{-3}	
		bulk	0.1 ± 0.01	
	on KCl	~30	0.26 ± 0.02	44
	on quartz	20→80	$(1\pm4)\times10^{-4}$	45
Pt				
	in gelatin	20	$(-4\pm2)\times10^{-4}$	46

[a] All atomic g-shift values are taken from Ref. 31 and all bulk values are taken from Ref. 29.

[b] Platelets.

[c] Different sites.

[d] Estimated from ΔH (questionable).

[e] Two different values exist in the literature.

[f] Asymetric signal.

represent a complete picture of the size-dependent g shift in CESR. In order to obtain a complete picture of the size-dependent g shift, *one must add up all size-dependent contributions, of which $\delta g_2'''(L)$ is only one.* It is nevertheless interesting to compare the results of calculating $\delta g_2'''(L)$ on the basis of both Kawabata's theory and the present model.

Owing to the translational symmetry of the lattice in an infinite crystal, the spin-orbit interaction $\mathscr{H}_{so}$ in that case has only nonzero matrix elements between states n and m whose wave vectors differ by a reciprocal lattice vector and whose energy differences are thus large. Thus, for a bulk metal, the energy denominators ϵ_{mn} which occur in Eq. (26) will be large and $\delta g_2'''(L)$ will be very small. On the other hand, in a small particle the translational symmetry of the lattice is broken and the matrix elements of $\mathscr{H}_{so}$ can be nonzero even for states which are close to each other in energy. Thus, the energy denominators in Eq. (26) can become small for a very small cluster and $\delta g_2'''(L)$ can become large. In Kawabata's[7] theory, this quantity is proportional to L^2 for clusters in which the quantum-limit conditions are satisfied. Thus in Kawabata's model $\delta g_2'''(L)$ approaches zero as $L \rightarrow 0$, increases as L^2 for small L, and then decreases again for large clusters when the pertubation theory used to derive Eq. (26) is no longer valid.

Using Eq. (26), we have numerically calculated $\delta g_2'''(L)$ in the single OSW approximation for a small cube of sodium. For this calculation, we have chosen the relation $L=(N_x'+1)a/2$, where as previously N_x' is the number of atoms along the edge of the bcc sodium lattice. In Fig. 4(a) we show (open circles connected by a solid curve) our results for the size dependence of the average spin-orbit interaction matrix elements which enter the calculation. In that same figure we show (dashed curve) Kawabata's[7] estimation of these same matrix elements, obtained by combining Eqs. (24) and (25), using $\delta(L) \propto L^{-3}$, and choosing the experimental value of -8×10^{-4} for $\delta g(\infty)$. It is remarkable that, despite the fact that these two theories are very different in their physical assumptions, they both predict a L^{-2} dependence of the average spin-orbit matrix elements. Their quantitative agreement is, however, probably fortuitous.

Our results in this approximation for $\delta g_2'''(L)$ are shown in Fig. 4(b) (solid curve), along with those of Kawabata (dashed curve). As may be seen from this figure, our model predicts that $\delta g_2'''(L)$ should be smaller than the value Kawabata predicts and that it should depend much less strongly on L than the L^2 dependence predicted by his model. This result may be related to the fact that for the cubic particle assumed in our single OSW calculation the electronic energy levels are highly degenerate. The average level separation is thus larger than for a particle with an irregularly shaped surface and is roughly proportional to L^{-2} rather than the L^{-3} obtained in Kawabata's model. Thus, in our calculation, the L dependence of the energy denominator sum in Eq. (26) ($\propto [\delta(L)]^{-2} \propto L^4$) roughly cancels out the L dependence of the square of the spin-orbit interaction matrix elements which occur in that equation ($\propto L^{-4}$) and the result is a roughly L-independent $\delta g_2'''(L)$. These qualitative arguments are in agreement with the general *trend* of the single OSW predictions shown in Fig. 4(b). It should be noted, however, that the level degeneracy in real small clusters is not as high as in a cubic particle. We thus estimate that our calculated $\delta g_2'''(L)$ corresponds to a minimum value.

It is certainly more correct to calculate the g-shift contribution $\delta g'''$ directly from Eq. (14), rather than consider its perturbation-theory approximation $\delta g_2'''(L)$. We have performed this calculation in the single OSW approximation and the results for a small cube of sodium, after some straightforward algebra, is

$$\delta g'''(L) = -\frac{48\Pi}{\Omega}\left[1-\frac{a}{L}\right] J_\Delta^2(\gamma_F)\left[1+\frac{\langle \gamma_{zF}^2\rangle}{\gamma_F^2}\right], \tag{27}$$

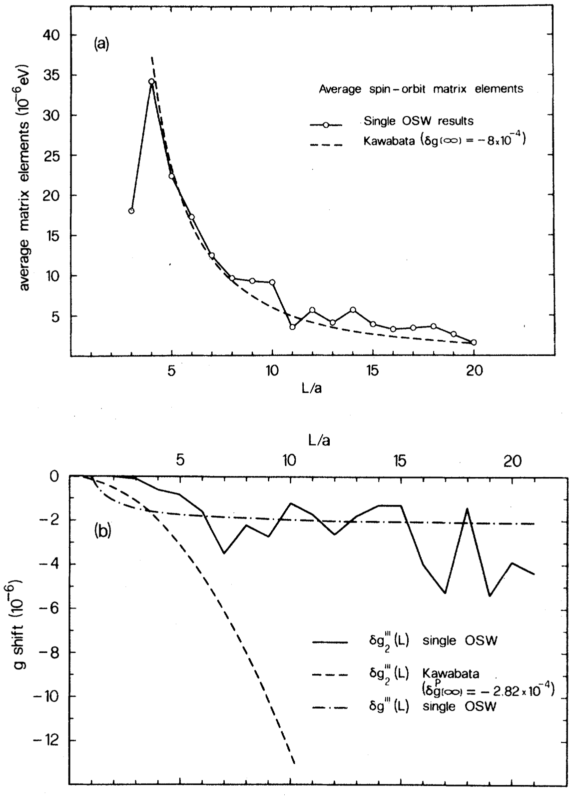

FIG. 4. (a) Average spin-orbit matrix elements for a sodium particle in the single OSW approximation (circles) and in Kawabata's theory (dashed curve) as a function of L/a for a bcc lattice structure with $L=(N_x'+1)a/2$ where N_x' is the number of atoms along a cube edge. (b) The Kawabata term in the g shift for a sodium particle; $\delta g_2'''(L)$ in the single OSW approximation (solid curve); $\delta g_2'''(L)$ in Kawabata's theory (dashed curve); and $\delta g'''(L)$ (exact expression) in the single OSW approximation (dot-dashed curve).

where we have used a bcc lattice with $L=(N_x'+1)a/2$, γ_{zF} is the z component of $\vec{\gamma}_F$, and J_Δ is defined in Eq. (16). As expected, this quantity is of second order in the spin-orbit coupling, since J_Δ is proportional to $\mathscr{H}_{\text{so}}$. For very small clusters Eq. (27) predicts that $\delta g'''(L)$ will approach zero, which is in agreement with Kawabata's estimation of $\delta g_2'''(L)$. However, unlike the expression obtained by Kawabata, Eq. (27) approaches a size-independent value for large L. If, as in the above calculations for $\delta g^p(L)$ and $\delta g''(L)$, we neglect the variation of $\vec{\gamma}_F$ with particle size, Eq. (27) can be written

$$\delta g'''(L) \cong \left[1-\frac{a}{L}\right]\delta g'''(\infty)\,, \tag{28}$$

where the bulk value, $\delta g'''(\infty)$, is numerically equal to -2.2×10^{-6}. The results obtained from Eq. (28) are shown in Fig. 4(b) (dot-dashed curve). They are in agreement with the average trend of the results for $\delta g_2'''(L)$ obtained with the same wave functions.

F. Summary and discussion

Using the bulk g-shift formalism we have investigated the size dependence of the CESR g shift in a model cubic particle of sodium using both single and multiple orthogonalized standing wave approximations for the conduction-electron wave functions. We have shown that, within this model, the main size-dependent contribution to the g shift comes from the δg^p term [Eq. (21)]. We have also calculated the size dependence of the g-shift contribution $\delta g''$ within the single OSW approximation [Eq. (22)]. Motivated by Kawabata's[7] treatment of the g shift in small metallic particles and by recent experiments which have indicated discrepancies with his theory, we have also investigated within our model the term which is denoted as $\delta g'''$ in the bulk g-shift formalism.[25] We have found that the g-shift term that Kawabata has calculated in his theory may be obtained from the bulk g-shift formalism by employing a perturbation-theory expansion of $\delta g'''$ to second order in the spin-orbit coupling. We find that the magnitude of $\delta g'''$ [Eq. (27)] is smaller for all particle sizes than that predicted by Kawabata and that its dependence on size is very different than the L^2 dependence that he predicts for very small particles. This difference could, however, be partly due to the large orbital degeneracy found in a small cubic particle.

From this analysis we conclude that the g shift in a small particle of sodium may be written

$$\delta g(L)=\delta g(a)\frac{\alpha a}{L}+\left[1-\alpha\frac{a}{L}\right]\delta g(\infty)+\delta g'''(L)\,, \tag{29}$$

where $\delta g'''(L)$ is very small, $\delta g(a)$ is the atomic g shift, $\delta g(\infty)$ is the bulk g shift, and α is of the order of unity.

The *size dependence* shown in this equation *is typical of a surface effect,* since the ratio of the surface area to the volume of a cube edge L is proportional to L^{-1}. This fact can be understood on the basis of the following analysis. In the atomic limit the δg^p contribution to the g shift will be zero (for sodium) since the outer $3s$ electron wave function will be orthogonal to the spin-orbit split $2p$ core wave functions. Thus, the g shift in this case will only consist of $\delta g(a)=\delta g'(a)+\delta g''(a)$.

In a bulk metal on the other hand, if one makes a plane-wave approximation for the $3s$ conduction-electron wave functions, they will not be orthogonal to the $2p$ states. A better approximation for bulk metals is an OPW approximation where the plane waves are orthogonalized to the core wave functions. In this case the $2p$ core states are mixed into the conduction-electron wave functions and this mixing results in a nonzero value for δg^p. One way of describing these results is to say that in the bulk crystal, each atom brings a contribution $\delta g^p(\infty)/N$ to the total δg^p shift, while the contribution of an isolated atom is zero. Furthermore, it is expected that the contribution of the atoms on the surface of a small particle to the small-particle g shift should be intermediate between the isolated atom and the inner atom (bulklike) contributions, since the surface atom environment is intermediate between that of an isolated atom and a bulklike atom. On the basis of this analysis, we are thus led to rewrite Eq. (29) in the following more general way:

$$\delta g(N,N_S)=(N-N_S)\frac{\delta g(\infty)}{N}+N_S\frac{\delta g(s)}{N}\,, \tag{30}$$

where N_S is the number of surface atoms, N is the total number of atoms in the particle, $\delta g(s)/N$ is the contribution of a surface atom to the total g shift, and $\delta g(s)$ tends towards $\delta g(a)$ for very small clusters.

We therefore believe that the discussion of the preceding paragraph, although quantitatively verified in this paper only for a small cubic particle of sodium, should not depend too strongly on the shape of the particle and should also remain qualitatively correct for other simple metals with essentially *s*-type conduction-electron wave functions. In the next section, we briefly review some of the existing small-particle *g*-shift data and compare it with this prediction.

IV. COMPARISON WITH EXPERIMENT

In Table III we summarize most of the existing *g*-shift data for small metallic particles; we have also included observed *g* shifts for single metal atoms and bulk metals. Both the atomic and the small-particle data must be interpreted with caution, since the clusters or atoms are usually either embedded in a matrix or deposited on a substrate. Thus, matrix or substrate effects could change the *g*-shift values from those expected for isolated small particles, particularly if the metal atoms combine chemically with those of the host or substrate. For example, Table III shows clearly that even for atoms embedded in a rare-gas matrix, the observed *g* shift is different than that of the free atom.

Both Smithard[35] and Gordon[36] have made detailed studies of CESR in small sodium particles produced by irradiation in NaN_3. In particular, they were able to measure the *g* shift of particles whose mean diameters range from 20 to 2000 Å and they report no change from the bulk *g*-shift value over this entire size range. Our model predicts, for example, *g*-shift changes from the bulk value of 20% and 8% for 20-Å and 50-Å particles, respectively. On the other hand, Kawabata's[7] theory predicts changes of 1% and 9% for the same particles. Unfortunately, all of these predicted changes are within the experimental error of the measurements. The *g* shift reported by Lindsay and Herschbach[34] for sodium trimers is probably influenced by the matrix and certainly influenced by the isosceles-triangle geometry in which the trimers were formed. Thus, only a detailed calculation which takes into account this geometry could predict its *g* shift. It is thus clear that more precise measurements of the *g* shift in small sodium particles are needed in order to check the predictions of the present theory.

The most detailed study of the evolution of the *g* shift as a function of size in small metallic particles has been done by Millet and Borel[40] for small magnesium particles embedded in a xenon matrix. Their measured *g* shifts for particles of mean diameters of 12, 17, 22, and 29 Å are given in Table III. Since the present theory should be qualitatively correct for small particles other than sodium, it is worthwhile to try to analyze their data using the general results found here and summarized in Eq. (29). Millet and Borel[40] have done this and have shown that their results can, indeed, be interpreted using Eq. (29) if one sets the $\delta g'''$ term equal to zero. In Kawabata's[7] theory this term would already be equal to -8×10^{-2} for 20-Å particles, in disagreement with the data. A detailed analysis of the data on the basis of Eq. (29) is carried out in Ref. (40).

The remaining *g*-shift values summarized in Table III are more difficult to interpret. However, it should be noted that, in qualitative agreement with Eq. (29), there is a tendency for the absolute values of the *g* shift in small particles to be smaller than the corresponding bulk values. Further experimental studies are certainly needed in order to obtain a clearer picture of the behavior of the *g* shift in small metallic particles. More generally, all aspects of CESR in small clusters, including relaxation times and linewidths, need further experimental study so that the behavior of such particles in the quantum size-effect regime can be better understood.

V. CONCLUSIONS

In this paper we have proposed a model for the conduction-electron wave functions in a small metallic particle of a simple metal. The proposed model is a finite size generalization of the standard orthogonalized plane wave[18] (OPW) formalism wherein the plane waves are replaced by standing waves in a box and these are then orthogonalized to all core states. The resulting wave functions are denoted as orthogonalized standing waves (OSW). We have applied this model in both the single and multiple OSW approximations to a small cubic particle of sodium. The multiple OSW approximation is, in principle, an exact method if we take into account self-consistent effects and include a sufficient number of single OSW's. Since we were not interested here in exact calculations, but in finding the trend of the *g* shift as a function of size, a non-self-consistent scheme was used. It appears, however, that the multiple OSW approximation gives reasonably good energy eigenvalues and charge densities, while the single OSW calculation can only be used if qualitative calculations are sufficient.

Using the OSW wave functions obtained for a small sodium particle, we have calculated the various contributions to the CESR g shift in such particles. We, however, have not calculated the so-called surface terms which are not negligible for sodium or other alkali metals.[14] The predicted results for the g shift as a function of particle size are summarized in Eq. (29), which was obtained on the basis of the single OSW approximation. Although we have done specific calculations only for sodium particles, we believe that Eq. (29) is qualitatively also valid for clusters of metals with essentially s-type conduction-electron wave functions. In these metals the g shift should thus increase in magnitude from its atomic value to its bulk value as the particle size increases. In the multiple OSW approximation we have only calculated the g-shift contribution δg^{p}. However, the results obtained for this quantity in that approximation are in qualitative agreement with the general behavior shown in Eq. (29). Furthermore, we have shown that the term in the g shift obtained by Kawabata[7] in his theory of CESR in small particles corresponds (in perturbation theory in the spin-orbit coupling) to the term denoted as $\delta g'''$ in the bulk g-shift formalism. We have evaluated this quantity in the single OSW approximation and have found the behavior shown in Fig. 4, which is in disagreement with Kawabata's predicted behavior for this term.

The existing experimental g-shift data on small metallic particles, although often difficult to interpret, are generally in qualitative agreement with the prediction made in Eq. (29).

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APPENDIX: DERIVATION OF THE KAWABATA g SHIFT FROM THE CONTRIBUTION $\delta g'''$

In this Appendix we show that the correction to the g shift for small particles which was calculated by Kawabata[7] on the basis of his theory can be obtained by starting with the term in the bulk g-shift formalism denoted as $\delta g'''$ and performing a perturbation-theory expansion, keeping only terms of second order in the spin-orbit interaction.

We begin with the bulk g-shift contribution $\delta g'''$ which has the form shown in Eq. (14) rewritten here in a slightly different form,

$$\delta g'''(n)=2\int \psi^{\dagger}_{n\uparrow}(\vec{r})(\sigma_z-1)\psi_{n\uparrow}(\vec{r})d^3r \ , \qquad \text{(A1)}$$

where we have labeled the electronic states by the quantum number n rather than [as in Eq. (14)] by the wave vector $\vec{k}$, σ_z is the usual Pauli spin matrix, and $\psi_{n\uparrow}(\vec{r})$ is the wave function corresponding to the highest occupied spin-up state, which is assumed here (and in Kawabata's[7] treatment) to be orbitally nondegenerate. Following Kawabata's perturbation treatment we write this wave function in the form

$$\psi_{n\uparrow}(\vec{r})=\psi^{(0)}_{n\uparrow}(\vec{r})+\psi^{(1)}_{n\uparrow}(\vec{r})+\psi^{(2)}_{n\uparrow}(\vec{r}) \ , \qquad \text{(A2)}$$

where $\psi^{(0)}_{n\uparrow}(\vec{r})$ is an eigenfunction of the crystal Hamiltonian in the absence of both spin-orbit coupling and the magnetic field and $\psi^{(1)}_{n\uparrow}(\vec{r})$ and $\psi^{(2)}_{n\uparrow}(\vec{r})$ are the first- and second-order perturbation terms in the spin-orbit coupling. Such a perturbation expansion is only valid if

$$\langle \psi^{(0)}_{n\uparrow} \,|\, \mathscr{H}_{\text{so}} \,|\, \psi^{(0)}_{m\sigma} \rangle < \epsilon^{(0)}_{mn} \ , \qquad \text{(A3)}$$

where $\mathscr{H}_{\text{so}}$ is the spin-orbit coupling Hamiltonian, σ is the spin index, and $\epsilon^{(0)}_{mn}$ is the energy difference between states m and n belonging to the eigenfunctions $\psi^{(0)}_{n\uparrow}$ and $\psi^{(0)}_{m\sigma}$. This inequality is equivalent to Kawabata's[7] quantum limit condition $\hbar/\tau < \delta$, where τ and δ are, respectively, the conduction-electron spin-lattice relaxation time and the average level separation of the discrete energy levels in the small particle. Both of these quantities are discussed in more detail in the text.

Given Eqs. (A1), (A2), and (A3) it is a simple exercise to show that the first-order term in $\mathscr{H}_{\text{so}}$ vanishes and that the second-order term is equal to

$$\delta g_2''' = -4 \sum_{m\neq n} \frac{\langle \psi^{(0)}_{m\downarrow} \,|\, \mathscr{H}_{\text{so}} \,|\, \psi^{(0)}_{n\uparrow} \rangle^2}{(\epsilon^{(0)}_{nm})^2} \ . \qquad \text{(A4)}$$

If Eq. (A4) is now averaged over states m near the Fermi surface, the result is the second term in Eq. (26) of the text. Thus, beginning with $\delta g'''$, Eq. (A1), and using the perturbation theory outlined here, the Kawabata[7] correction to the g shift is easily obtained.

The evaluation of $\delta g_2'''$ in the single OSW approximation is a rather long but straightforward calculation if we assume that the one-electron spin-orbit Hamiltonian can be written as

$$\mathscr{H}_{\mathrm{so}} = \sum_{\vec{R}_j} \xi(\vec{r}-\vec{R}_j)\,\vec{l}_j\cdot\vec{s}\ , \tag{A5}$$

where $\vec{l}_j$ is the orbital angular momentum of the electron centered on site $\vec{R}_j$ and $\xi(\vec{r})$ depends on the gradient of the potential $V(\vec{r})$. By using Eqs. (A4) and (A5), along with the wave functions of Eq. (2) of the text, the quantity $\delta g_2'''$ can then be calculated.

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