Density Functional Theory of Crystal Field Quasiparticle Excitations and the *Ab Initio* Calculation of Spin Hamiltonian Parameters

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We show, by carefully examining the change of total energy in constrained variational calculations using the local spin density approximation, that crystal field excitations in normal rare earths are quasiparticles composed of a $4f$ excitation plus its associated cloud of shielding conduction electrons. Total energy calculations, which properly exclude the self-interaction of the nonspherical part of the $4f$ densities, are then used to calculate crystal field energies and the corresponding spin Hamiltonian parameters of TmSb and PrSb, accurately from first principles. [S0031-9007(97)04150-1]

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The electronic structure and magnetic moments of transition metals and their compounds may be calculated to great accuracy from the variational principle for the total energy of the entire electron density provided by density functional theory [1] in the local spin density approximation (LSDA) [2] to the correct functional. The localized $4f$ shell in the rare-earth metals and their compounds, which provide most of the magnetism in the periodic table, is entirely different in nature. The magnetic moments of the $4f$ shell are obtained first from Russel-Saunders coupling in the atomic limit leading to a highly correlated degenerate ground state with full rotational symmetry and a conserved total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$. In the solid state the full rotational symmetry is reduced to the point group symmetry of the crystal and the degenerate ground state splits into groups of crystal electric field (CEF) levels. When exchange interactions between the $4f$ shells on different atoms are added, a complete description of the ground and low lying states is obtained through a spin Hamiltonian [3]. The strength of this standard model [4] of the rare earths is that it is soundly based upon symmetry considerations, and the dynamics of low lying excitations is therefore described correctly. We do not consider anomalous rare earths, notably cerium and its compounds where the standard model breaks down due to the onset of itinerancy, in which case the origin of the CEF is more complex [5].

Since the parameters in the spin Hamiltonian arise from the electronic environment in the solid they are dependent upon the conduction electron density. In the standard model the exchange interactions between localized $4f$ states are transmitted via the conduction electron polarization, and the nonspherical potential is believed to be the crystal field. Analysis, usually based on first or second order perturbation theory, is used to eliminate the degrees of freedom of the conduction electrons by relating them to the spin Hamiltonian parameters which are normally treated as adjustable [4]. In order for theory to have predictive power it is desirable to be able to calculate these parameters from first principles. That constrained LSDA calculations produce excellent results for exchange interactions in rare earths and their compounds has already been demonstrated [6–8]. Unfortunately, attempts to calculate the CEF spin Hamiltonian parameters [9,10] have, despite recent progress [11–13], been only moderately successful. We suggest that the reason is not the technicalities of the calculations themselves but the incomplete treatment of conduction electron shielding.

When density functional theory is applied to the rare earths the conduction electron degrees of freedom are retained and the total energy of the entire solid is minimized *subject to the constraint that the* $4f$ *occupation numbers are fixed and that the* $4f$ *states obey Russel-Saunders coupling* [7,14]. The ground and low lying excited states of the $4f$ shell are normally [15] the lowest energy states of a given symmetry. Therefore the total energy of each may be calculated subject to the above constraints plus the constraint that the density and spin density have the correct symmetry. It should then in principle be possible to calculate the spin Hamiltonian parameters *ab initio* from CEF excitation energies which are obtained from differences in the total energy. In practice we have found that constrained total energy calculations involving the $4f$ states reveal severe problems with LSDA applied to highly correlated $4f$ states, the culprit being the self-interaction of the nonspherical part of the $4f$ density with itself.

The total energy of the electrons in the field of the nuclei is a functional of the total electron density

$$E[n] = T_s[n] + E_N[n] + E_H[n] + E_{\mathrm{xc}}[n], \quad (1)$$

where the contributions are the kinetic energy, electron-nuclei interaction energy, Hartree electron-electron interaction energy, and exchange-correlation energy, respectively. Since each crystal field level has a unique electron density and since the total energy in Eq. (1) is a functional of the density, it is possible to apply Eq. (1)

directly to calculate the splittings between CEF levels. We have found that application of Eq. (1) using LSDA fails and the ultimate evidence for its breakdown is that it does not yield degenerate CEF levels in the atomic limit. The reason for this is that if the nonspherical $4f$ density corresponding to a crystal field state is placed in a spherical environment (as is the case for a free atom) the total energy in LSDA will depend upon the nonspherical part of the $4f$ density due to its Hartree interaction with itself. The total energies for two different crystal field states in an atom will therefore differ in LSDA, *even when the rest of the electron density is spherical,* since the self-interaction of the nonspherical part of the $4f$ density breaks the spherical symmetry and reduces the degeneracy of the ground state. This is clearly an artifact of the local density approximation which allows the $4f$ states to erroneously bootstrap their own crystal field and which is closely related to the difficulties encountered with the calculation of multiplet energies [16]. In Russel-Saunders coupling the internal interactions between the $4f$ states are already included by the construction of **J** and the degeneracy of the $4f$ ground state should be $2\mathrm{J} + 1$. We have found that straightforward use of Eq. (1) yields CEF splittings of, for instance, a Pr or a Tm atom which are bigger than the measured CEF splittings in PrSb and TmSb [17].

The cure to this problem is to remove the culprit, the self-interaction of the nonspherical part of the $4f$ charge density at a given site. The first two terms in the right-hand side of Eq. (1) remain unchanged. If the total density is written $n(\mathbf{r}) = \bar{n}(\mathbf{r}) + n_{4f}^{\mathrm{ns}}(\mathbf{r})$, where $n_{4f}^{\mathrm{ns}}(\mathbf{r})$ is the nonspherical part of the $4f$ charge density, the Hartree energy becomes

$$E_H[n] = \frac{1}{2}\int \frac{\bar{n}(\mathbf{r})\bar{n}(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} + \int \frac{\bar{n}(\mathbf{r})n_{4f}^{\mathrm{ns}}(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}, \qquad (2)$$

where a third term, $n_{4f}^{\mathrm{ns}}(\mathbf{r})n_{4f}^{\mathrm{ns}}(\mathbf{r}')$, appearing in LSDA is explicitly excluded. Similar changes must be made to the exchange and correlation energy which becomes, when E_{xc} is expanded in a Taylor series to first order in n_{4f}^{ns},

$$E_{\mathrm{xc}}[n] = \int \bar{n}(\mathbf{r})\epsilon_{\mathrm{xc}}[\bar{n}]\,d\mathbf{r} + \int n_{4f}^{\mathrm{ns}}(\mathbf{r})\mu_{\mathrm{xc}}[\bar{n}]\,d\mathbf{r}, \qquad (3)$$

where ϵ_{xc} is the exchange-correlation energy per electron of a uniform electron gas of density n and μ_{xc} is $d(n\epsilon)/dn$.

The Hartree plus exchange-correlation potential for non-$4f$ states becomes

$$V_H = \int \frac{\{\bar{n}(\mathbf{r}) + n_{4f}^{\mathrm{ns}}(\mathbf{r})\}\,d\mathbf{r}}{|\mathbf{r}-\mathbf{r}'|} + \mu_{\mathrm{xc}}[\bar{n}] + n_{4f}^{\mathrm{ns}}(\mathbf{r})\,\frac{\delta\mu_{\mathrm{xc}}[\bar{n}]}{\delta\bar{n}}, \qquad (4)$$

whereas for $4f$ states it is

$$V_H^{4f} = \int \frac{\bar{n}(\mathbf{r})\,d\mathbf{r}}{|\mathbf{r}-\mathbf{r}'|} + \mu_{\mathrm{xc}}[\bar{n}]. \qquad (5)$$

When the appropriate substitution for the kinetic energy is made in Eq. (1) the total energy becomes

$$E = \sum_i n_i\epsilon_i - \frac{1}{2}\int \frac{\bar{n}(\mathbf{r})\bar{n}(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} + \int \{\epsilon_{\mathrm{xc}}[\bar{n}] - \mu_{\mathrm{xc}}[\bar{n}]\}\bar{n}(\mathbf{r})\,d\mathbf{r} - \int n_{4f}^{\mathrm{ns}}(\mathbf{r})\,\frac{\delta\mu_{\mathrm{xc}}[\bar{n}]}{\delta\bar{n}}\,\bar{n}(\mathbf{r})\,d\mathbf{r}. \qquad (6)$$

We have imposed a check on the applicability and numerical integrity of Eq. (6) by demanding that the crystal field levels become degenerate in the atomic limit (in practice this was done by making bulk calculations for a very large lattice constant). This criterion was found to be satisfied for all of the calculations reported here, and the degeneracy of the Russel-Saunders ground state was assured.

At the correct lattice constant the difference in total energy between the crystal field states contains two contributions. First there is the charge transfer contribution in a compound, normally known as the lattice contribution to the nonspherical potential because it arises from other sites. Second there is the contribution from the interaction between the nonspherical part of the $4f$ density at a given site and the nonspherical part of the non-$4f$ (primarily conduction) electron density. The latter contribution includes the effects due to redistribution of the conduction electron density in reaction to a change of $4f$ density in a crystal field excitation, which we have found to be not small. A crystal field excitation should therefore be correctly viewed as a $4f$ excitation plus its concomitant shielding conduction electron charge cloud, i.e., as a quasiparticle.

To capture this picture we have performed self-consistent calculations where, as described above, the self-interaction of the nonspherical part of the $4f$ density was removed. The calculations were made for two rare-earth compounds, PrSb and TmSb. TmSb was chosen since it is well documented that it is an ideal exchange-free compound [17,18], and PrSb was chosen to investigate the influence of the number of $4f$ electrons on the applicability of our theory. The calculations were made for the observed NaCl structure and lattice constant. The valence electron density and potential were allowed to take any geometrical shape in the calculations, and great care was taken for the expansion of the density, potential, and sampling of the Brillouin zone [19]. The results which are reported here were obtained using the local density approximation, but we note that results obtained from the generalized gradient approximation [20] were very similar. The $4f$ electrons were constrained to give trivalent rare-earth (Re) ions, which means that there were

2 and 12 open shell $4f$ electrons for PrSb and TmSb, respectively. The $4f$ electron density was expressed as a radial part (calculated self-consistently) multiplied by a term ensuring the correct asphericity of each CEF state. The radial density was obtained using Eq. (5), but we also investigated the effect of the self-interaction correction [21] for the radial part of the density upon the calculated CEF levels, which we found to be small. For each CEF level all the electron states were obtained self-consistently, being allowed to relax to the change in density involved in a CEF excitation, with the only constraints being the occupation of the $4f$ state and its asphericity.

In Fig. 1 we compare our results with measurements. The theory reproduces both the ordering of the levels as well as the magnitude of the level splittings. Typically the calculated levels differ from measured ones by less than 1 meV, with the largest error being some 30% for the Γ_5 level of PrSb. In this figure we also show our results based upon the standard CEF model (data labeled Model), which neglects the effect of valence electron density shielding of the CEF levels, producing excitation energies which are typically one-half of those measured and calculated self-consistently. The limitation of the latter approach is well documented [11–13].

In order to further demonstrate the importance of the valence electron shielding we show in Fig. 2 the difference in valence electron density of TmSb in the Γ_1 and Γ_3 states. This plot shows how the valence electron density changes when the $4f$ charge density is modified from a shape associated with the Γ_1 CEF state to a shape associated with the Γ_3 CEF state. The lobes elongated vertically and horizontally represent a surplus of electron charge, whereas the lobes which are rotated with 45° represent a charge deficiency. Figure 2 thus shows that shielding and relaxation effects of the valence electron states are important, and this conclusion is quantified by Fig. 1.

To examine the effect of conduction electron shielding in greater detail and to isolate the physical origin of CEF energy level splitting, we imagine the nonspherical $4f$ density corresponding to a crystal field state to be a small test charge added to the conduction electron density. The nonspherical $4f$ density in each crystal field state is an external constraint imposed upon the conduction electron system, and the conduction electron density in the crystal relaxes to shield the impurity and minimize the total energy. This process must also occur in the free atom where we obtained a degenerate ground state, and the lower panel of Fig. 2 shows the calculated change in conduction electron density in this case. Clearly the relaxation of the atomic conduction electron density is similar to that of the crystal, but for the atom the shielding is larger and exactly sufficient to retain rotational symmetry. The rotational degeneracy of the ground state of the atom may therefore be obtained either by imposing a spherical conduction electron density or by allowing the conduction electron density to relax, the latter being the state of lowest energy. For the bulk the nonspherical crystal boundary conditions prevent the outer conduction electron density from relaxing as in the free atom which removes the spherical symmetry of the ground state. The quasiparticle then has a finite excitation energy.

In standard crystal field theory the conduction electron density is obtained in the presence of a spherical $4f$ density, and the crystal field parameters arise from the interaction between the nonspherical part of this conduction electron density and the nonspherical part of the $4f$ density in first order perturbation theory. Provided that any kinetic energy changes associated with a crystal field transition, which are included in a total energy calculation, are small, this should give a good estimate of that part of the crystal field excitation energy due to the interaction of the $4f$ part and the nonspherical conduction electron density induced by the crystal. The accuracy of such an estimate is aided by the fact that the energy of the self-consistent calculation is at a variational minimum and any induced changes in density will make a contribution to the energy which cancels to first order. However, the contribution from the interaction between the conduction electron part of the quasiparticle and the nonspherical conduction electron density induced by the crystal is omitted.

In summary, we have shown that it is possible, by means of a total energy formalism, to calculate crystal

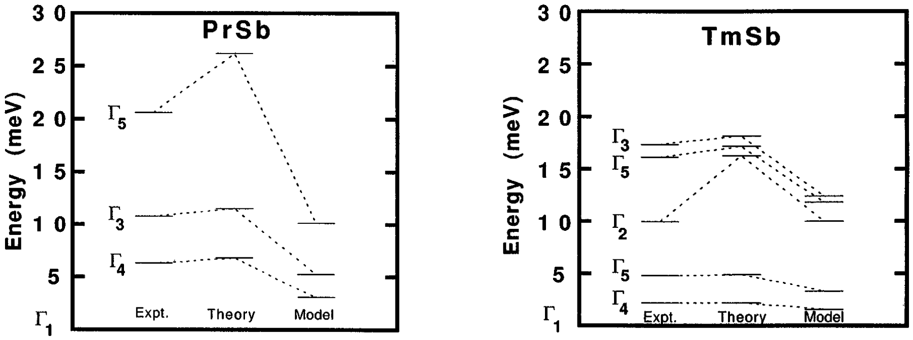

FIG. 1. Experimental and theoretical crystal field splittings of PrSb and TmSb. The calculations were based on Eq. (7) (data labeled theory) as well as from an approach described in Ref. [11] (data labeled Model). Both for TmSb and PrSb the ground state is the Γ_1 state which is at zero energy.

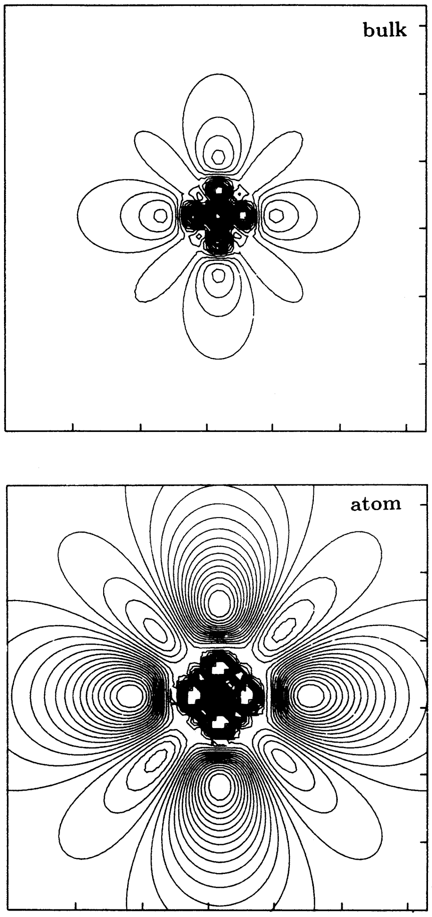

FIG. 2. Charge density contour around the Tm atom of the difference in shielding valence electron density of TmSb when there is a transition from the Γ_1 to the Γ_3 CEF states. The upper panel shows data for the crystal and the lower panel for the atom.

field excitation energies or, equivalently, CEF spin Hamiltonian parameters from first principles with a modified LSDA theory, where the self-interaction of the nonspherical part of the $4f$ density is explicitly excluded. The self-interaction energy correction for the nonspherical part of the $4f$ density is more important in this context than the normal self-interaction correction for the radial part of the $4f$ density, since the former is at least as large as the crystal field excitation energies. We have demonstrated that crystal field excitations should be viewed as quasiparticle excitations where the change of the localized $4f$ density is intimately connected with a valence screening charge and that the conventional view that crystal field excitation energies in metals are due to the static electrostatic field alone is much to simple.

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