

Application of an on-site self-interaction-corrected method to Ce and the α -Ce surface

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A restricted implementation of the self-interaction-corrected density-functional method is described, and applied to the α - γ transition in fcc Ce and to the α -Ce surface. The method, based on a full-potential linear muffin-tin orbital method, does not allow full minimization of the local-density approximation–self-interaction-corrected energy functional, but does contain all of the fundamental energetics of electron localization. This allows an essentially parameter-free, yet economical, determination of whether localization is energetically favored. Application of this method to the α - γ transition in Ce achieves good agreement with other self-interaction-corrected calculations, while the Ce surface provides a good demonstration of the utility of the method. The calculations predict a monolayer of localized f states on the surface, and the resulting surface relaxation is examined. [S0163-1829(99)01332-6]

Rare-earth and actinide materials often exhibit a highly correlated electronic structure, characterized primarily by varying degrees of f -state localization. This localization, and changes in the localization, affect a number of observable properties, including structural properties. One well-studied example is the isostructural α - γ transition in fcc cerium, in which the material undergoes a 17% volume collapse from the high-volume γ phase to the lower-volume α phase. While the nature of the transition has been the subject of some controversy,¹ one proposed theory is that this is a Mott transition, with the Ce $4f$ changing from a localized to delocalized, hybridized state. Another example in Ce is the surface of α -Ce, which photoemission data² suggest are more γ -like in electronic structure, with a localization of those f states at or near the surface.

Standard LDA (local-density approximation) calculations fail to describe such transitions between delocalized and localized states, and it is well known that this is due to the failure of the LDA energy functional to obtain the decrease in Coulomb energy that results from localization, which in turn is closely related to the LDA's inclusion of substantial self-interaction energies. Perdew and Zunger³ have introduced a self-interaction-corrected (SIC) density-functional method, and several recent calculations of rare-earth^{4,5} and actinide⁶ properties have applied this SIC method with good success. In particular, SIC calculations of the α - γ transition in Ce have reproduced the volume collapse, and other properties, fairly well. Use of the SIC method has been limited, however, by the difficulty of its full incorporation into calculations of extended systems. The SIC method described here, while approximate in some respects, contains all of the essential physics of localization, and is easily implemented within an all-electron density-functional program, with essentially no cost in computational requirements. (This method is in essence quite similar to a method, described in Ref. 7, that has been developed and applied largely to crystal-field splittings and magnetic properties. There are, however, several technical differences between the two methods.)

In the self-interaction-corrected density-functional method,³ the ground-state density is obtained, as in the

Kohn-Sham method, by minimizing an energy functional with respect to variations in a set of occupied, orthonormal, one-electron states. The SIC energy functional is, however, made explicitly interaction free for each orbital, with the result that the states are determined using an orbital-dependent effective potential; $V_i(\mathbf{r}) = V_{\text{LDA}}(\mathbf{r}) - V_{\text{SIC}}(\mathbf{r})$, where the correction to the LDA effective potential, V_{SIC} , is the Hartree and exchange-correlation potential calculated from the i th state's density. This correction is zero for extended states, but may be substantial for localized states.³ The computational difficulties arise from the fact that any localized states are not Bloch states (and should, in principle, be calculated using a supercell approach); and from the requirement that all of the orbitals, while calculated from different effective potentials, must still form a set of orthogonal states.^{3,8}

The approximate SIC method employed here is a variation on the "f in core" approach to f localization, and makes the assumption that the localized f states are confined to one atomic site. In this case, the form of the localized f states can be obtained reasonably well by calculating the f states as are the core states, by solution of the Dirac equation in a spherically averaged potential. This f in core technique for localizing the f states has been in use for some time,⁸⁻¹¹ and has been shown capable of predicting equilibrium volumes and bulk moduli in systems where it is assumed that the f 's are localized, including fcc Ce. This is because f in core does, of course, remove those f states from the bond-forming valence band. It is usually accompanied by complete removal of f basis functions from the valence basis set. (A method similar to the f in core method has been applied to the actinides in Ref. 12. An LDA+ U approach to actinides has also been investigated.¹³)

Simply putting the f 's in core in LDA calculations has two central drawbacks, which are addressed by the present method. First, without any self-interaction correction, the calculated energy does not contain the decrease in electrostatic energy obtained by localization, and so cannot be used to predict whether or not localization is favorable. This deficiency is easily addressed by including the self-interaction correction for the core f 's much as in atomic calculations,³

using the spherically averaged density of a core f state to determine the SIC potential and energy.

The second drawback is the all or nothing aspect of the technique, wherein if even one localized f state is occupied, the valence states are forced to lose all $4f$ character. Here a method was developed which allows moving one f electron at a time from valence to core. This is accomplished by including in the valence Hamiltonian, for each occupied f core state $|f_i\rangle$, the projection operator $E_0|f_i\rangle\langle f_i|$, where E_0 is an arbitrary large energy (200 Ry here), so that the corresponding f state is effectively unavailable for occupation by the valence states. This partial retention of f character in the valence basis set (absent in the method of Ref. 7) was found to have a non-negligible influence on the calculated results, including equilibrium volumes and crystal-field splittings. Thus this self-interaction corrected f in core technique contains all the major features of localization: the localized f is taken out of bonding hybridizations; the decrease in electrostatic energy is included; and all of the occupied states remain (largely) orthogonal, without extraneous constraints.

This method does not, however, contain a variational determination of the SIC localized state: The f states are eigenstates of a spherically symmetric potential (with nonspherical corrections as described below), not the periodic LDA potential plus SIC potential. Nonetheless, as long as orthogonal states are occupied, a correct evaluation of the SIC-LDA energy functional will provide an upper bound for the energy of the localized system, and so can be used to search for the onset of localization. Since the localized states are not variational, their construction—that is, the choice for the spherically symmetric potential—is to some extent arbitrary. In this work the spherically averaged effective potential was used out to the point where this function reached a maximum, typically at about half of the nearest-neighbor distance (and outside the muffin-tin radius). Beyond that radial distance, the potential was kept constant. In addition, a smooth potential barrier was included beyond this point. This was done not only (as in the light actinides, to be described in a later publication) to provide bound states, but also to prevent overlap with neighboring localized states, and so maintain orthogonality between them. For Ce, the f states are fairly well contained near the parent nuclear site, and so the shape, and even to some extent the existence, of the barrier did not have a significant effect upon calculated results.

As in other SIC implementations,⁴⁻⁷ another question to be addressed concerns which f states to localize. Here the localized states were allowed to be any linear combination of the 14 members of the f multiplet, and the final choice was made through minimization of the total energy, examining the most physically motivated linear combinations, including total angular-momentum eigenstates and members of irreducible representations of the point group. (For a singly occupied f state, or for any occupation which is less than a full representation of the point group, the projection operator included in the one-electron Hamiltonian does not possess the full O_h point-group symmetry of the lattice. The set of \mathbf{k} points were chosen accordingly, but only O_h compatible terms were kept in the potential and density.) Finally, the interaction of the localized f states with the nonspherical components of the potential were included through first-order perturbation theory, $\Delta E = \sum_i \langle f_i | \delta V(\vec{\mathbf{r}}) | f_i \rangle$; however,

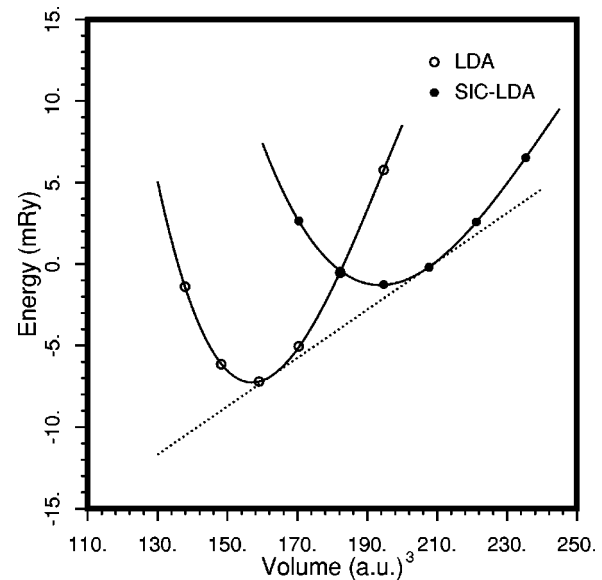


FIG. 1. Calculated energy of fcc cerium as a function of atomic volume, for both the LDA calculation and the SIC-LDA calculation with one localized f electron per atom. The dotted line is the tangent to both curves.

the nonspherical components of the localized f -states electron density were not included in the self-consistent electron density, and therefore not in the state's self-interaction correction.

This simplified SIC method was applied to the α - γ phase transition in bulk fcc Ce, and to the (001) surface of α -Ce. A full-potential linear muffin-tin orbital (LMTO) method¹⁴ was used; with the $5s$ and $5p$ semicore states included in the valence set; with $5s$, $5p$, $6d$, $7s$, and $7p$ “double- κ ” basis functions and a “single- κ ” $4f$ basis function; and with inclusion of spin-orbit matrix elements. As in other SIC calculations of the α - γ transition,^{4,5} the low volume α phase is assumed to be represented by the standard LDA calculation, and the LDA energy versus volume curve is shown in Fig. 1. The calculated equilibrium lattice constant is 8.57 a.u., about 6% smaller than the experimental value of 9.16 a.u.¹ While this difference is larger than usually obtained by LDA calculations, it appears to be in good agreement with some other full-potential calculations.⁹

Figure 1 also shows the energy of the SIC-LDA calculation with one localized f electron, representing the larger volume γ phase. An examination of the relative energies obtained by localizing total angular-momentum eigenstates confirmed that the spin-orbit interaction dominated other effects, with $j=5/2$ and $j=7/2$ states being split in energy by about 25 mRy. Within the $j=5/2$ multiplet, linear combinations giving members of the Γ_7^- doublet and Γ_8^- quartet were examined. Here, while the “bare crystal-field” splitting (the expectation value of the nonspherical components of the potential), was on the order of 1 mRy, the final energies were much closer, due to the differing cost in energy of projecting Γ_7^- or Γ_8^- functions out of the valence set. The total energy was 0.2 mRy lower, at equilibrium, for Γ_7^- occupation, and these are the energies given in Fig. 1. The equilibrium lattice constant is again about 6% smaller than the experimental value (a calculated 9.18 a.u., compared with the γ -Ce experimental¹ value of 9.75 a.u.), with the result that the

volume collapse is in good agreement with experiment. The calculated volume collapse is 18.6%, while the experimental value is roughly 17%. Other SIC calculations^{4,5} of the α - γ transition have obtained volume collapses of around 24%. It is not clear to what extent this small difference between calculated results is due to the "on-site" approximation, or other considerations, such as the fact the earlier SIC calculations have been based on atomic-sphere-approximation implementations of the LMTO method, rather than a full-potential method.

The negative slope of the tangent line shown in Fig. 1 is the predicted pressure required for the zero-temperature transition, and the calculated value is equal to -22 kbar. This is to be compared to other (variational) SIC values of -1 kbar,⁴ and $+17$ kbar,⁵ and an experimental value of -7 kbar.¹ These values are all relatively close, corresponding to uniform shifts in the SIC-LDA energy curve on the order of 5 mRy and again it is not possible to distinguish the contribution of the on-site approximation versus full-potential and other numerical considerations. It can be concluded that, for Ce, the current method provides a good reproduction of other implementations of the self-interaction correction.

The efficiency of the current method allows the examination of more complicated systems, of which localization at the Ce surface provides a good example. The (001) surface of α -Ce was calculated using a nine-layer, repeated slab, constructed with the calculated bulk equilibrium lattice constant. The slab calculation was performed three times: with no f localization, with the surface monolayer given localized f states, and with the surface and subsurface layers localized. The three relative total energies for the unrelaxed surface clearly indicate that localization at the surface is favored, but only for the surface layer, and not for subsurface layers. The unrelaxed surface with one localized layer is 17 mRy (per

surface atom) lower in energy than that with no localization, and 21 mRy lower in energy than the two-localized-layer surface. The finding that localization is energetically favored for just one layer is in agreement with a LDA plus orbital-polarization examination of the same system,¹⁵ and in agreement with experiments² which indicate localization occurs at the surface, although for an undetermined number of layers.

The increased volume of the γ phase implies that the localized surface layer is under compression, and it has been suggested¹⁵ that this might result in surface reconstruction. Here, only the effect on surface relaxation has been examined, for both the delocalized and the one-localized-layer calculations. Both were found to have inward relaxations, common to many metallic fcc systems, with the delocalized surface relaxation being found to be -5.2% of an interlayer spacing, and for the localized system, an inward relaxation of -3.3% . The respective relaxation energies were 1.9 and 0.7 mRy per surface atom.

In conclusion, a simplified form of a self-interaction-corrected calculation has been developed which is easy to implement within an all-electron LDA method, and is computationally economical. It allows examination of whether on-site electron localization is energetically favored, and also allows some means of including partial localization since, in systems with multiple f occupation, one electron at a time may be moved from localized to delocalized states. For the α - γ transition in Ce, the method was able to reproduce earlier SIC results in which the on-site restriction was not imposed, obtaining comparable values for both the volume collapse and transition pressure. Application to the α -Ce surface shows that the SIC description of localization in Ce predicts a γ -like monolayer at the (001) surface.

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