8 SCIENTIFIC HIGHLIGHT OF THE MONTH: Local Self-Interaction Correction of a Scattering Resonance: The Atom in Jellium Model

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Local Self-Interaction Correction of a Scattering Resonance: The Atom in Jellium Model

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Abstract

The atom in jellium model describes a single atom interacting with an infinite homogenous electron gas. It can be thought of as the simplest first principles model which includes all of the essential physics of the Anderson impurity model, namely one or more localized atomic-like states hybridized with a continuum of free electron band states. For example in the case of rare earth elements, such as Ce, one can use the atom in jellium model to examine the valence state of the atom as a function of the jellium density, or r_s. This in turn can be used to understand in simple terms the valence transitions which might occur in bulk materials, for example as a function of pressure. In this highlight we present calculations of a Ce atom in jellium, in which we compare the LSDA results with those of the Local Self-Interaction Correction (LSIC). The LSIC approximation of density functional theory was introduced by Lüders et al.[*Phys. Rev. B*, 71:205109, 2005], and it extends the original self-interaction correction theory to apply the correction to long-lived resonances as well as to bound states. Using the atom in jellium model for Ce we show explicitly how this applies to the $4f$-like states of the Ce atom in jellium. The LSIC has solutions which correspond to different numbers of these f states treated as either SI-corrected or not. This causes these electrons to localize, which within the effective medium theory (EMT) corresponds to a change in the valence of cerium metal as a function of Wigner-Seitz radius.

1 Introduction

The atom in jellium model describes a single atom interacting with an infinite electron gas. It is simply characterized by two parameters, namely the nuclear charge, Z, and the jellium density n_0, or r_s, where $\frac{4\pi}{3}r_s^3 n_0 = 1$. The model has been extensively studied in the past, usually within the local spin density approximation (LSDA), as an illustration of chemical bonding of an atom to a metallic host [1–3]. In this context the key result of the calculation is the immersion energy $E_{imm}(n_0)$, which is the energy of the atom in jellium system compared to the atom in free space and the jellium without the atom. This immersion energy is one of the key ingredients in the semi-empirical Embedded Atom Method (EAM) [4]. Effective medium theory (EMT) provides a fully first principles theory of total energies of solids, in which each atom is viewed as embedded in an effective jellium provided by the electron clouds of its neighbours [5]. This theory gives a very good overall description of the trends in Wigner-Seitz radii across the $3d$ [6] or $4d$ [7] transition metals.

In this highlight we examine the atom in jellium model from a quite different point of view. Namely, it can be thought of as the simplest first principles model which includes all of the essential physics of the Anderson impurity model [8]. This model is the central model in "quantum impurity" problems, including the theory of the Kondo effect. It is characterized by one or more localized atomic states, with an energy ϵ_f and an on-site repulsion U, which are hybridized with a free electron band of states $\epsilon_{\mathbf{k}}$, by the matrix element $V_{\mathbf{k}}$,

$$\hat{H} = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c^{+}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \epsilon_f f^{+}_{\sigma} f_{\sigma} + U \hat{n}_{f\uparrow} \hat{n}_{f\downarrow} + \sum_{\mathbf{k}\sigma} V_{\mathbf{k}} \left(c^{+}_{\mathbf{k}\sigma} f_{\sigma} + h.c. \right), \tag{1}$$

where $c^{+}_{\mathbf{k}\sigma}$ is the usual creation operator for electrons in band states and f^{+}_{σ} is the creation operator for the localized state, with $\hat{n}_{f\sigma} = f^{+}_{\sigma} f_{\sigma}$. As well as modelling a single atomic impurity in a metallic host, this model is central to Dynamical Mean Field Theory (DMFT) [9]. In DMFT the free particle band of states $\epsilon_{\mathbf{k}}$ is replaced with a suitably chosen effective medium, obtained self-consistently from the many-body solution of the Hamiltonian of Eq. 1. Implemented together with LDA+U or other means to estimate the Anderson model parameters this is now one of the most widely used first principles approaches to the theory of d and f-electron metals and their compounds [10, 11].

Our motivation for studying the atom in jellium model is to find an alternative route to an effective quantum impurity problem, i.e. without mapping onto the Anderson impurity problem explicitly, and without invoking an additional parameter, U. Although effective Hubbard parameters, U, can be estimated from constrained density functional theory [12] our aim is to solve the atom in jellium model directly without requiring this additional step. For example, one possible approach is to solve the atom in jellium model directly using quantum Monte Carlo (QMC). We have recently shown that this approach is feasible, at least for an atom embedded in a finite size jellium sphere. For a Hydrogen in jellium we were able to obtain reasonable immersion energies, $E_{imm}(n_0)$, using a Variational-QMC approach based on a trial wave function previously used by Sottile and Balone [13]. Our results [14] show a minimum in $E_{imm}(n_0)$ of about $1eV$ at a jellium density of about $n_0 = 0.0025 a_B^{-3}$. In contrast the LSDA result for the same system is a minimum of about $2eV$ at the same density. We interpret this as evidence for overbinding in LSDA compared to the more exact QMC results.

Unfortunately the QMC approach is currently too expensive to apply to a more interesting case, such as rare earth atoms embedded in an electron gas. For these atoms we have applied the Local Self-Interaction-Correction (LSIC) method, first developed by Lüders *et al.* [15]. In particular we have demonstrated explicitly the ability of the LSIC method to self-interaction correct both bound states and states within scattering resonances. This then leads to a theory which can describe valence transitions between different valence states of the rare earth atom as a function of jellium density, or Wigner-Seitz radius within the EMT theory [5]. The remainder of this highlight describes the LSIC method, and its application to a Ce atom in jellium.

2 Local Self-interaction Correction (LSIC)

The self-interaction correction (SIC) [16] approximation to density functional theory (DFT) was proposed by Perdew and Zunger to ensure that the exchange correlation functional becomes exact for a single electron in a bound state. Other widely used approximations, such as the local spin density approximation or the generalized gradient approximation (GGA) do not obey this constraint, and therefore make an error when applied to a single electron. The Perdew-Zunger SIC adds a correction term to the LSDA, which subtracts the unphysical Hartree self-interaction of each single electron generalized Kohn-Sham orbital spin density, $n_{i\sigma}(\mathbf{r})$ and the corresponding erroneous LSDA exchange and correlation energy, $E_{xc}[n_{i\sigma}, 0]$. The resulting energy functional is a functional of the generalized Kohn Sham orbital densities, $n_{i\sigma}(\mathbf{r})$, and becomes exact when only one electron bound state is occupied. The original Perdew-Zunger SIC functional was shown to improve significantly the descriptions of atoms, for example giving the correct asymptotic $-1/r$ form of the Kohn Sham potential $V(\mathbf{r})$, and providing improved ionization energies and electron affinities. For systems where all the Kohn Sham states are extended the SIC correction vanishes and so the functional again becomes equal to the usual LSDA (or GGA).

The application of SIC to bulk periodic crystals leads to an improved description of systems with tightly localized electron states, such as 3d transition metal oxides and the lanthanide and actinide f-electron metals [17]. In these cases the SIC functional allows electronic states to be either band-like or localized, and both kinds of states are treated together within the same *ab initio* approach. In general the self-consistent minimization of the total energy functional leads to solutions with different numbers of localized states, and the lowest energy solution found is taken as the global ground state. If no states are found to be localized the method is equivalent to standard LSDA. These different localization states can be interpreted physically as representing different chemical valence states of the d or f shell states. In particular for Cerium it was found that the isostructural transition between the α and γ phases arose naturally from the SIC methodology as a valence transition between trivalent and tetravalent Ce [18].

An important feature of the original SIC formulation by Perdew and Zunger was that the SIC should vanish for the case of extended quantum states. However, recently Lüders *et al.* [15] proposed an extension of the SIC to strongly bound resonances. They argued that it is reasonable to apply the SIC for resonances, provided that the time for which the electron is bound in the resonance (the Wigner delay time) is longer than other characteristic timescales in the quantum many-body scattering problem. In practice this new formulation of SIC, named local-SIC (LSIC), has the advantage of being compatible with the multiple scattering KKR approach to electronic structure calculations. Unlike the original Perdew Zunger formulation of SIC, it can also be applied for finite temperature calculations, and combined with the coherent potential approximation (CPA) for disorder and with the disordered local moment (DLM) model of finite-temperature magnetism [19]. The LSIC has been successfully applied to a wide range of different systems, including the α and γ phase transition of Ce [15].

We first show that the LSIC functional proposed and developed by Lüders et al. [15] can be readily adapted to the case of an atom in jellium. In the original formulation of SIC, the correction would be applied to all the bound states, but not to any extended states, as for example in the embedded atom calculations of Puska and Nieminen [20]. However, demonstrably within the model, the electron density due to a resonance in the continuum states is just as well-localized as the density due to a discrete state. Therefore it is reasonable to assume that the self-interaction for such a resonance does not vanish, and so the corresponding self-interaction energy terms for this density should also be subtracted from the LSDA energy functional. In what follows we shall demonstrate this with explicit calculations.

3 LSDA solution of an atom in jellium

We consider an atom of atomic number Z, embedded in a uniform jellium of background electron density n_0. Within the LSDA the ground-state solution is obtained by solving the self-consistent Kohn-Sham (KS) equations

$$\left(-\frac{1}{2}\nabla^2 + V^\sigma(r)\right)\phi_i^\sigma(\mathbf{r}) = E_i^\sigma \phi_i^\sigma(\mathbf{r}) \tag{2}$$

where, assuming spherical symmetry, the potentials are

$$V^\sigma(r) = \int \frac{\Delta n(r')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' - \frac{Z}{r} + V_{xc}^\sigma(n^\uparrow(r), n^\downarrow(r)) - V_{xc}(\frac{n_0}{2}, \frac{n_0}{2}). \tag{3}$$

where $\Delta n(r) = n(r) - n_0$ is the atom induced electron density. In principle the Kohn-Sham potentials, $V^\sigma(\mathbf{r})$, and spin-densities, $n^\sigma(\mathbf{r})$, may become non-spherical, however in the work described below we have imposed spherical symmetry on the spin densities, and hence the KS equations reduce to the radial Schrödinger equations. The final term in Eq. 3 defines the potential energy to be zero far from the ion.

The total energy of the atom in jellium is defined by

$$\begin{aligned} E_{tot} \;=\; & \sum_{n,l,\sigma}(2l+1)E_{nl}^\sigma + \int_0^{E_F} E\Delta n(E)dE - \\ & \sum_\sigma \int n^\sigma(r)V^\sigma(r)d\mathbf{r} + \\ & \int \left(\frac{1}{2}\int \frac{(\Delta n(r'))}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' - \frac{Z}{r}\right)(\Delta n(r))\,d\mathbf{r} + \\ & E_{xc}\left[n^\uparrow(r), n^\downarrow(r)\right] - E_{xc}\left[\frac{n_0}{2}, \frac{n_0}{2}\right] \end{aligned} \tag{4}$$

where the E_{nl}^σ are the KS eigenvalues of the atom induced bound states ($E_{nl}^\sigma < 0$) of quantum numbers n and l, and $\Delta n(E)$ is the atom-induced density of states in the continuum ($0 < E < E_F$, where E_F is the Fermi energy of the jellium). The Hartree and exchange-correlation energy terms are defined to subtract out the (infinite) energy of the jellium background, ensuring that

$E_{tot} = 0$ in the absence of the atom. Note that the continuum eigenvalue energy term above can be re-written in terms of the scattering phase-shifts, $\delta_l^\sigma(E)$ for angular momentum channels l,

$$\int_{E=0}^{E_F} E\Delta n(E)dE = \frac{1}{\pi}\sum_{\sigma,l}(2l+1)E_F\delta_l^\sigma(E_F) - \frac{1}{\pi}\sum_{\sigma,l}(2l+1)\int_0^{E_F}\delta_l^\sigma(E)dE. \tag{5}$$

4 LSIC solution for an atom in jellium

In the LSIC formalism, we minimize the energy functional

$$\begin{aligned} E_{tot} &= \sum_{l,m,\sigma} E_l^\sigma + \frac{1}{\pi}\sum_{\sigma,l}(2l+1)E_F\delta_{l,m}^\sigma(E_F) - \\ &\frac{1}{\pi}\sum_{\sigma,l,m}\int_{E=0}^{E_F}\delta_{l,m}^\sigma(E)dE - \sum_\sigma\int n^\sigma(r)V^\sigma(r)d\mathbf{r} + \\ &\int\left(\frac{1}{2}\int\frac{(n(r)-n_0)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \frac{Z}{r}\right)(n(r)-n_0)\,d\mathbf{r} + \\ &E_{xc}\left[n^\uparrow(r), n^\downarrow(r)\right] - E_{xc}[\frac{n_0}{2},\frac{n_0}{2}] - \\ &\sum_\alpha\left(\frac{1}{2}\int_{r=0}^{R^\alpha}\int_{r'=0}^{R^\alpha}\frac{n_{SIC}^\alpha(r)n_{SIC}^\alpha(r')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_{xc}[n_{SIC}^\alpha(r),0]\right) \end{aligned} \tag{6}$$

where n_{SIC}^α is the density of the channel α, which in this case is one of the $l = 3$, m, σ channels for which the SI-correction is applied. α denotes the spin and angular momentum quantum numbers, and in the case of bound states also the principal quantum number. In this functional, the radii R^α are either set equal to the neutral sphere radius [5], or are set by the condition

$$\int_{r=0}^{R^\alpha} n_{SIC}^\alpha(r)d\mathbf{r} = 1 \tag{7}$$

We show below that our results are independent of this choice.

Minimizing the energy functional with respect to the orbitals gives the following generalized KS equations for the SI-corrected electrons:

$$\left(-\frac{1}{2}\nabla^2 + V_{SIC}^\alpha(r)\right)\phi_{SIC}^{\alpha,(b.s)}(\mathbf{r}) = E_{SIC}^\alpha\phi_{SIC}^{\alpha,(b.s)}(\mathbf{r}) \tag{8}$$

for the bound-state solution, and

$$\left(-\frac{1}{2}\nabla^2 + V_{SIC}^\alpha(r)\right)\phi_{SIC}^{\alpha,(s.s)}(k,\mathbf{r}) = \frac{k^2}{2}\phi_{SIC}^{\alpha,(s.s)}(k,\mathbf{r}) \tag{9}$$

for the scattering-state solutions. The quantity $n_{SIC}^\alpha(r)$ is then obtained as the density contributions from the bound and scattering state SIC solutions,

$$n_{SIC}^\alpha(\mathbf{r}) = |Y_{lm}(\theta,\phi)|^2 R^\alpha(r)^2 + \frac{1}{2\pi^2}|Y_{lm}(\theta,\phi)|^2\int_0^{k_f} k^2 R^\alpha(k,r)^2 dk, \tag{10}$$

where $\phi_{SIC}^{\alpha}(\mathbf{r}) = Y_{lm}(\theta, \phi)R^{\alpha}(r)$ for both bound and scattering states in a given SIC angular momentum channel, $lm\sigma$. As illustrated in Fig. 1, the first term refers to the negative energy contribution while the second one accounts for positive energy contributions within a given SIC channel. In the case of a partially filled sub-shell, we spherically average the corresponding SIC densities $n_{SIC}^{\alpha}(\mathbf{r})$.

For the non-SI-corrected electrons we obtain the LSDA KS equations

$$\left(-\frac{1}{2}\nabla^2 + V^{\sigma}(r)\right)\phi_i^{\sigma}(\mathbf{r}) = E_i^{\sigma}\phi_i^{\sigma}(\mathbf{r}) \tag{11}$$

which also contain bound and scattering state solutions.

5 Self-interaction correction of scattering resonances for Ce in jellium

In order to test whether the above generalization of SIC adds useful physical insight, we consider the case of a cerium atom embedded in a jellium host. Cerium is an interesting case because of its mixed valency, having different valence states depending on the $4f$ orbital occupation. In a jellium host the LSIC formalism allows the $4f$ state of Ce to be either bound or a scattering state. In fact we find both possibilities occur as we vary the jellium density n_0. This is illustrated in Fig. 1 which shows the phase-shifts $\delta_{lm}^{\sigma}(\epsilon)$ for a cerium atom in jellium, with one electron SI-corrected, for two background densities of the jellium. For the low density of $n_0 = 0.0014a_B^{-3}$ ($r_s \sim 5.5a_B$), the SIC potential generates a bound-state, whereas for a high density $n_0 = 0.04a_B^{-3}$ ($r_s \sim 1.8a_B$) the SIC potential generates a resonance in the continuum. The figure shows that in both cases the f-wave phase shift jumps by π in the SI-corrected channel, lm. In Fig. 1 one can see that the phase shifts for the non-SI-corrected f channels show a sharp resonance located just above the Fermi energy, while the d channels show a broad resonance above ϵ_F and the s and p channels are non-resonant. In a pure LSDA calculation all of the f states would have been resonant above ϵ_F, corresponding to a pinning of the partially filled $4f$ shell states at the Fermi energy. The SIC allows one (or more) of the f states to become pulled below the Fermi energy, giving a full electron charge in a $4f$ pseudo-atomic state. It is this ability to treat localized and extended states with different orbital dependent effective potentials, $V_{SIC}^{\alpha}(\mathbf{r})$, which is at the heart of the success of SIC in treating narrow band materials [17]. One can see from Fig. 1 that the LSIC also has this ability, treating some of the Ce $4f$ states as atomic-like and SI-corrected, while treating the remaining $4f$ states in the same way as standard LSDA.

The key feature of the LSIC is that it treats bound states and resonances on an equal footing. Therefore there is no discontinuity in the generalized KS potentials $V_{SIC}^{\alpha}(\mathbf{r})$ when a bound state becomes a scattering resonance. This is confirmed in Fig. 2 where we plot the f resonance energy for a single LSIC corrected state in Ce as a function of jellium density n_0. The range of densities corresponds to typical metallic values of r_s. At low densities the f state is bound, crossing over smoothly to a sharp resonance which moves up and gradually broadens as the jellium density increases. However, at some jellium density the total energy corresponding to a delocalised f electron, i.e. the LSD energy, becomes more favourable and hence the ground state.

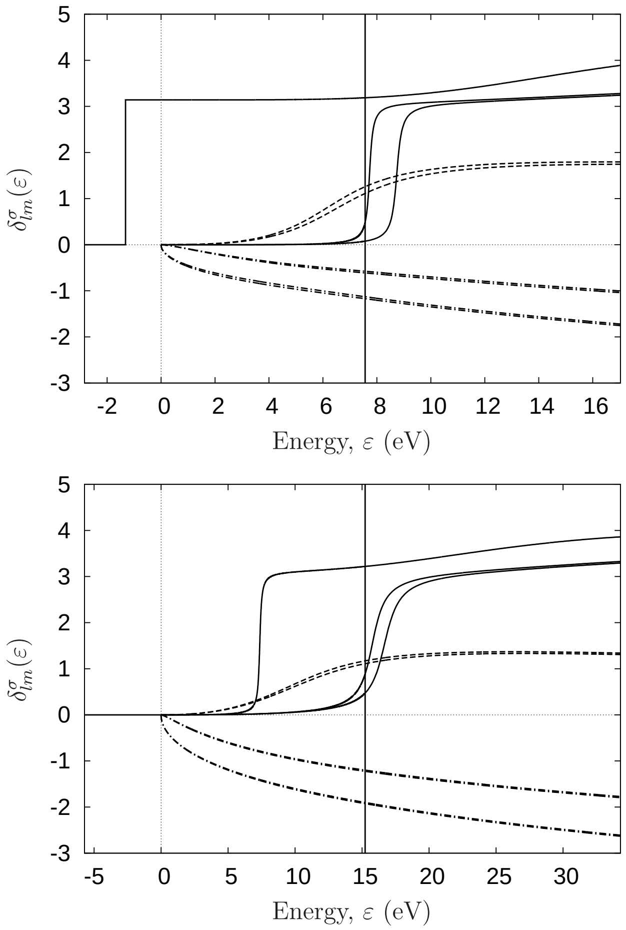

Figure 1: Phase-shifts for cerium in jellium with one electron SI-corrected. The two background densities are: (a) $0.0014a_B^{-3}$, and (b) $0.032a_B^{-3}$. In the first case the SIC potential binds an electron and in the second the SI-corrected state appears as a resonance in the scattering states. Here the solid lines are f channel phase shifts (both SI-corrected and not corrected), the dashed lines are d-channels, and the dot-dashed lines are s and p channels. Splitting of up and down spin states is also visible in the d and the non SI-corrected f channels.

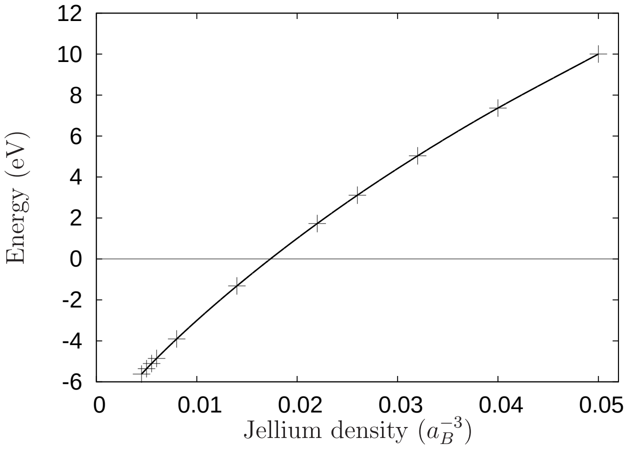

Figure 2: Position of the bound-state/resonance generated by the SIC potential as a function of the background density of the jellium. The system is a cerium atom in jellium with one electron SI-corrected.

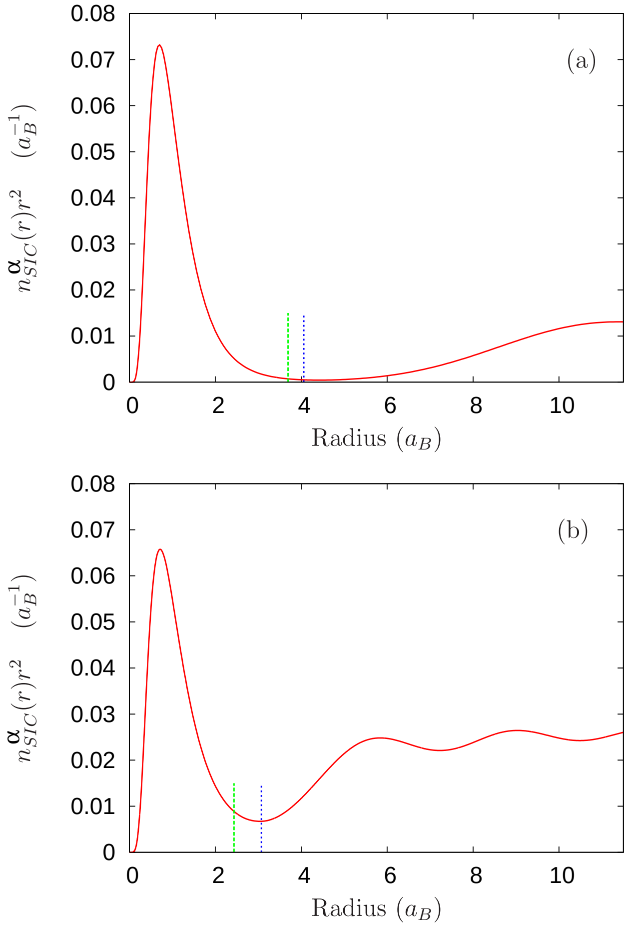

Figure 3: The SIC corrected orbital density $n^{\alpha}_{L}(r)$ is plotted for a cerium atom in jellium with one electron SI-corrected for two background densities, $0.0055a_B^{-3}$ (a) and $0.04a_B^{-3}$ (b). The straight lines indicate the neutral sphere radius (furthest left) and the radius at which the total integrated SIC charge equals one (as defined by Eq. 7).

The physical justification of LSIC requires that the orbital density $n^{\alpha}_{SIC}(\mathbf{r})$ contains one electron within the atomic radius R^{α}, as expressed in Eq. 7. To demonstrate that this is indeed the case we show in Fig. 3 the orbital density, spherically symmetrized, for the case of a bound or resonant SI-corrected $4f$ channel, for two jellium densities $0.0055a_B^{-3}$ and $0.04a_B^{-3}$. For the lower of the two densities the SIC potential localizes a bound-state, while for the higher of the two the SIC potential generates a resonance, as can be seen from Fig. 2. One can see that the orbital density is similar whether the SIC corrected channel contains a bound state or a scattering resonance. Hence the self-interaction for the case of the resonance is just as large as for the bound-state, therefore demonstrating the need for an energy functional which can include scattering states in the SI- correction.

Fig. 3 also shows two possible definitions of the atomic sphere R for the Ce in jellium. One can take either the "neutral sphere radius" of Effective Medium Theory (EMT) [5], defined as the radius for which the atom-induced electron density $\Delta n(\mathbf{r})$ integrates to the nuclear charge Z, or define a radius R^{α} for which Eq. 7 is satisfied exactly for the SI-corrected f channel. In practice it is clear from Fig. 3 that these two definitions give essentially identical results. It is also clear from the figure that the total channel density $n^{\alpha}_{SIC}(r)$ for $r < R^{\alpha}$ contains the localized atomic-like part of the density and very little of the extended jellium-like part. Therefore it does not matter in detail whether one includes only the part of the density associated with the bound state or resonance, or includes all of the density up to ϵ_F within that $L = lm$ channel, as given in Eq. 7.

6 Effective Medium Theory of Ce metal

In the EMT, each atom in a solid is regarded as sitting in an electron density set up by the density tails of all of the other atoms in the solid. The only input parameter in the EMT is the atomic number, Z. The theory has been successfully put to use in the calculation of cohesive properties of solids, amongst other uses. In particular, the theory reproduces trends in the experimental lattice constants, bulk moduli and cohesive energies across the periodic table [5,6,20].

In the EMT, the cohesive energy of the solid is written as

$$\Delta E[n, v] = \sum_i E_c(\bar{n}_i) + \Delta E_{1-el} \tag{12}$$

where

$$E_c(\bar{n}) = E_{imm}(\bar{n}) + \bar{n} \int_{r=0}^{r=s} \left(\int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \frac{Z}{r} \right) d\mathbf{r} \tag{13}$$

Here $\Delta n(\mathbf{r})$ is the atom-induced density. The second term is attractive and has the effect of lowering $E_c(\bar{n})$. It can be viewed as the attraction of the sum of the density tails from all other cells ($\bar{n}$) with the Hartree potential from cell a_i.

The ΔE_{1-el} term is the sum of the change of the one-electron energy eigenvalues when we go from the homogeneous electron gas to the real host. This change occurs because of covalent bonding, hybridisation and effects due to wavefunction orthogonalisation. A number of ways

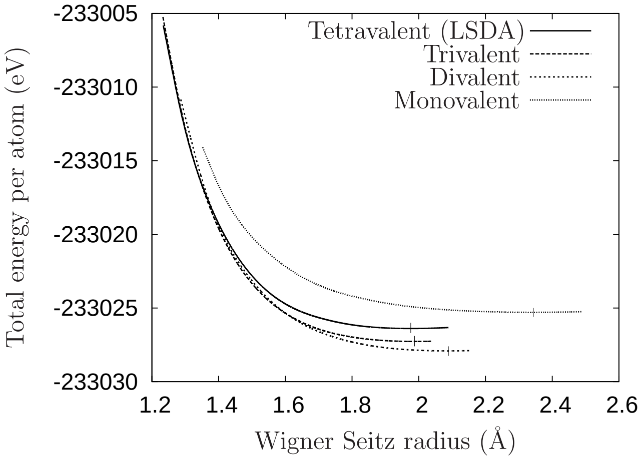

Figure 4: Total energy per atom plotted against the Wigner-Seitz radius (EMT neutral sphere radius) for different choices of the exchange-correlation functional. SI-correcting two electrons, which corresponds to a valence of two in the full solid, gives the lowest energy.

have been proposed to include this term [21–25], however in our calculations we will neglect this term. With this term neglected, $E_c(\bar{n})$ is the cohesive energy per atom.

The procedure in EMT is to solve for some arbitrarily chosen $\bar{n}$, the self-consistent problem of an atom in a homogeneous gas in order to obtain $\Delta n(\mathbf{r})$ and then evaluate $E_c(\bar{n})$. One then varies $\bar{n}$ in order to minimise $E_c(\bar{n})$. This minimum value of $E_c(\bar{n})$ is then the cohesive energy per atom of the solid, and the corresponding value of neutral sphere radius, R^α, is the Wigner-Seitz radius as predicted by the theory.

Fig. 4 shows our results for the total energy of a bulk Ce metal calculated using the effective medium theory (EMT) from our LSIC atom in jellium results. The different curves correspond to: standard LSDA with no SIC correction (tetravalent Ce), one f state SIC corrected (trivalent Ce), two f states corrected (divalent Ce) and three states corrected (monovalent Ce). The curves are plotted as a function of the effective Wigner Seitz atomic radius, obtained within the EMT theory. The fcc-γ phase of Ce is believed to be trivalent, [18] corresponding to one localized f state. Our calculations predict the minimum energy Wigner Seitz radius for trivalent Ce to be 1.99 $\mathring{A}$, in very good agreement with the Wigner-Seitz radius of 2.02 $\mathring{A}$ fcc-γ phase Ce.

One can see in Fig. 4 a series of crossings between the different valence states as a function of the Wigner-Seitz radius. At the smallest Wigner-Seitz radius the LSDA tetravalent state is lowest in energy, crossing over to trivalent and then divalent at the radius is increased. In terms of the phase diagram of Ce this would imply a series of valence state transitions under pressure. If the α-γ transition in bulk Ce is viewed as a crossing between trivalent and tetravalent states, then our EMT results give a small volume “collapse” of a few % in volume, but one which is much smaller than found experimentally or in previous SIC calculations [15, 18]. Nevertheless the SI-corrected calculation appears to capture the essential physics of the valence transition. However our global minimum energy state is the divalent one, with a larger radius of about 2.09$\mathring{A}$, rather than the expected trivalent state. It is most likely that this discrepancy arises from the omission of the covalent terms in the EMT theory, ΔE_{1-el}. The spherical symmetrization of the LSDA and SIC-charge densities is also a possible problem, since recent results of Stengel and Spaldin show a substantial contribution to the energy from the non-spherical terms. [26] We leave further investigation of these important questions to future work.

7 Conclusions

We have demonstrated that the LSIC approach is necessary to correctly treat the self-interaction of resonances in the system of an atom in jellium. We have shown that the electron density corresponding to a resonance is just as localized as that due to a bound-state, and therefore this resonance should also be corrected for in the LSIC energy functional. Using the LSIC, we have shown that as we increase the background density of the jellium, a bound-state of the LSIC potential will increase in energy and will eventually become a scattering state resonance. This resonance will continue to increase in energy as the background density is increased further. This is in contrast with the Perdew-Zunger SIC approach. In this approach, when the electron in the SIC channel enters the continuum of scattering states, it will no longer be treated for its self-interaction and so will become extended and will not form a resonance.

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References

[1] M.J. Stott and E. Zaremba, Phys. Rev. B **22**, 1564 (1980).

[2] J.K. Norskov and N.D. Lang, Phys. Rev. B **21** 2131 (1980).

[3] M.J. Puska, R.M. Nieminen, M. Manninen, Phys. Rev. B **24** 3037 (1981).

[4] M.S. Daw, Phys. Rev. B 39, 7441 - 7452 (1989)

[5] K.W. Jacobsen,J.K. Norskov and M.J. Puska, Phys. Rev. B **35**, 7423 (1987).

[6] U. Yxklinten, J. Hartford, and T. Holmquist. Phys. Scripta, 55:499, (1997).

[7] A.I. Duff, *"First Principles Investigation into the Atom in Jellium Model System"*, PhD thesis, University of Bristol (2007).

[8] P.W. Anderson, Phys. Rev. **124** 41 (1961).

[9] A. Georges, G. Kotliar, W. Krauth and M.J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).

[10] K. Held *et al.*, *Realistic investigations of correlated electron systems with LDA+DMFT* Psi-k highlight, Newsletter 56 - April (2003).

[11] G. Kotliar *et al.* Rev. Mod. Phys. **78**,865 (2006).

[12] P. H. Dederichs, S. Blügel, R. Zeller, and H. Akai Phys., Rev. Lett. **53**, 2512 (1984).

[13] F. Sottile and P. Ballone, Phys. Rev. B **64** 045105 (2001).

[14] A.I. Duff and J.F. Annett, Phys. Rev. B **76**, 115113 (2007).

[15] M. Lüders, A. Ernst, M. Däne, Z. Szotek, A. Svane, D. Ködderitzsch, W. Hergert, B. L. Gyorffy, and W.M. Temmerman. Phys. Rev. B **71**, 205109, (2005).

[16] J. P. Perdew and A. Zunger. Phys. Rev. B **23** 5048 (1981).

[17] W.M. Temmerman, A. Svane, Z. Szotek and H. Winter, in *Electronic Density Functional Theory: Recent Progress and New Directions*, Eds. J.F. Dobson, G. Vignale and M.P. Das (Plenum NY 1998.), p. 327.

[18] Z. Szotek, W.M. Temmerman and H. Winter, Phys. Rev. Lett. **72** 1244-1247 (1994).

[19] I.D. Hughes, M. Däne, A. Ernst, W. Hergert, M. Lüders, J. Poulter, J.B. Staunton, A. Svane, Z. Szotek, and W.M. Temmerman, *"Lanthanide contraction and magnetism in the heavy rare earth elements"*, Nature **446**, 650 (2007).

[20] M. J. Puska and R. M. Nieminen, Phys. Rev. B, **43** 12221 (1991).

[21] O. B. Christensen, K. W. Jacobsen, J. K. Nørskov, and M. Manninen. *Phys. Rev. Lett.*, 66:2219, 1991.

[22] P. Nordlander, S. Holloway, and J. K. Nørskov. *Surf. Sci*, 136:59, 1984.

[23] J. K. Nørskov. *J. Chem. Phys.*, 90:7461, 1989.

[24] L. Hansen, P. Stoltze, K. W. Jacobsen, and J. K. Nørskov. *Phys. Rev. B*, 44:6523, 1991.

[25] U. Yxklinten, Y. Andersson, and B. I. Lundqvist. *Phys. Rev. Lett*, 72:2302, 1994.

[26] M. Stengel, N.A. Spaldin, *"Self-interaction correction with Wannier functions"* arXiv:0706.3210.