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Configuration dependence of hopping matrix elements in the Anderson model

O. Gunnarsson and O. Jepsen

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, West Germany

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In *ab initio* calculations of the hopping matrix element V in the Anderson model, it is found that V^2 may vary by a factor of 2–8 for Mn, Ce, and U compounds when different relevant configurations are used. We give a prescription for which configuration to use in an *ab initio* calculation of V, and we make a corresponding modification of the hopping term in the Anderson model, which can easily be implemented in methods for solving the model. We discuss how this influences the calculated properties of Ce compounds.

The Anderson model[1] has frequently been used for describing systems with localized states interacting with extended states. Examples of such systems are rare-earth, actinde, and many transition-metal compounds. Traditionally, the parameters of the Anderson model have been treated as fitting parameters to be determined from some experiment(s).[2] Recently there have, however, been a number of calculations of the parameters for $4f$ systems,[3] dilute magnetic semiconductors[4,5] and high-T_c superconductors,[6] using the local spin-density approximation.[7] In this approach, one is then confronted with the question of which configuration to use in the calculation of the localized wave function. As an example, we consider an Mn impurity in CdTe, where the Mn $3d$ orbital is the localized state. In the ground-state calculation the d^5 configuration dominates, but the d^6, and possibly the d^4, configurations also play a role. In valence photoemission, a $3d$ electron may be removed, making the d^4 configuration important and in core-level photoemission a core hole is created. The localized orbital (here $3d$ orbital) strongly depends on the number of localized and core electrons used in generating the potential for which the orbital was calculated. This orbital strongly influences the hopping matrix element, V. Actually, V^2 can be related[5] to a potential parameter, $\tilde{\Delta}$, in the linear muffin-tin orbital (LMTO) method[8]

$$V^2 \sim \tilde{\Delta} \approx \frac{s}{2}[\phi_l(C,s)]^2 . \tag{1}$$

Here $\phi_l(C,s)$ is the value of the localized orbital at the Wigner-Seitz radius s. The localized orbital with the angular momentum l is obtained by solving the radial Schrödinger equation for the energy C, the "position of the resonance," corresponding to the boundary condition that the logarithmic derivative at s is $-l-1$. Results for $\tilde{\Delta}$ for Mn in CdTe, α-Ce, and metallic U are shown in Table I. The table illustrates that $\tilde{\Delta}$ depends strongly on the configuration used in calculating ϕ. For Mn, we find that adding one $3d$ electron increases $\tilde{\Delta}$ by about 50%–70%, and creating a core hole, keeping the number of $3d$ electrons fixed, reduces $\tilde{\Delta}$ by more than a factor 2. For U, the dependence is slightly weaker, while it is even stronger for Ce. It is, therefore, crucial to find a prescription for how to choose the appropriate configuration in the calculation of $\tilde{\Delta}$. In the generalization of the Anderson model normally used for core spectroscopies,[2] the number of core holes is a conserved quantity, and it is clear how many core electrons should be included in a given calculation. This is, however, not obvious for the number of $3d$ electrons. If, for instance, we are interested in a hopping matrix element involving the d^n and d^{n+1} configurations, should the localized orbitals then be calculated for the d^n, d^{n+1}, or some intermediate configuration?

To discuss this issue, we introduce a simple model with two orbitals. By forming a linear combination of these orbitals, we can obtain a localized solution with a radial extent which is adjusted as the configuration is changed. We then discuss the calculation of the relevant hopping matrix elements within this model and map it back onto the normal Anderson model. This gives us a simple prescription for how to choose the appropriate configuration in the calculation of $\tilde{\Delta}$ for a given matrix element.

The localized orbital $\phi_l(r,n_l)$ is determined by the radial Schrödinger equation with the potential $v(r,n_l)$. The potential is calculated for the occupation number, n_l, of the localized orbital, and we use the boundary condition that the logarithmic derivative at the Wigner-Seitz radius is $-l-1$. The wave function $\phi_l(r,n_l)$ is normalized. We now choose some reference occupation n_l^0 and denote the corresponding solution

$$\phi_l^0 \equiv \phi_l(r,n_l^0) . \tag{2}$$

TABLE I. The potential parameter $\tilde{\Delta}$ for different configurations of Mn, Ce, and U in non-spin-polarized calculations. The localized orbital is $3d$ (Mn), $4f$ (Ce), and $5f$ (U), and we consider a core hole in the $1s$ (Mn), $3d$ (Ce), and $4f$ (U) orbital. The occupancy of the localized and core orbital is n_l and n_c, respectively. We have introduced n_l^0, which is 5 (Mn), 1 (Ce), or 3 (U), and n_c^0 , which is 2 (Mn), 10 (Ce), or 14 (U). All energies are in Ry.

n_l	n_c	Mn	Ce	U
n_l^0-1	n_c^0	0.0051	0.0008	0.0072
n_l^0	n_c^0	0.0085	0.0019	0.0091
n_l^0+1	n_c^0	0.0129	0.0038	0.0112
n_l^0	n_c^0-1	0.0040	0.0005	0.0053
n_l^0+1	n_c^0-1	0.0067	0.0011	0.0069

We also introduce the derivative

$$\phi_l^1 \equiv A\frac{\partial}{\partial n_l}\phi_l(r,n_l)\bigg|_{n_l=n_l^0}, \tag{3}$$

where A is chosen so that ϕ^1 is normalized. From the normalization of $\phi_l(r,n_l)$ it follows that ϕ^0 and ϕ^1 are orthogonal. In Fig. 1, we show these orbitals calculated for the Mn d^5 configuration, i.e., $n_{3d}^0=5$. The orbitals ϕ^0 and ϕ^1 will be used as basis functions for our two-orbital model. For the potential used in Fig. 1, the expectation values of the corresponding Hamiltonian are $\varepsilon_0=-0.45$ Ry and $\varepsilon_1=1.68$ Ry, for $|\phi^0\rangle$ and $|\phi^1\rangle$, respectively. We introduce the derivative of the potential

$$v^1(r)\equiv\frac{\partial}{\partial n_l}v(r,n_l)\bigg|_{n_l=n_l^0}. \tag{4}$$

For Mn in CdTe, we have the matrix element

$$\langle\phi^1|v^1|\phi^0\rangle\equiv\tilde{U}=0.16. \tag{5}$$

We now temporarily introduce a simple, generalized Anderson Hamiltonian with two localized orbitals ϕ^0 and ϕ^1.

$$\begin{aligned}H={}&\sum_{k,\sigma}\varepsilon_k n_{k\sigma}+\sum_{i=0}^{1}\varepsilon_i\tilde{n}_i+\sum_{i=0}^{1}\sum_{k,m,\sigma}(V_{ikm}\psi_{im\sigma}^{\dagger}\psi_{k\sigma}+\text{H.c.})+\tfrac{1}{2}U_{00}\tilde{n}_0(\tilde{n}_0-1)\\&+\tfrac{1}{2}U_{11}\tilde{n}_1(\tilde{n}_1-1)+U_{01}\tilde{n}_0\tilde{n}_1+\tilde{U}\sum_{m,\sigma}(\psi_{1m\sigma}^{\dagger}\psi_{0m\sigma}+\text{H.c.})(\tilde{n}_0+\tilde{n}_1-1),\end{aligned} \tag{6}$$

where

$$\tilde{n}_i=\sum_{m,\sigma}n_{im\sigma}-(n_l^0-1)\delta_{i0}. \tag{7}$$

Here ε_k are the energies of the extended states $|k\sigma\rangle$, where k is some quantum number and σ is the spin. The energies of the localized states are ε_i, and m is the azimuthal quantum number. V_{ikm} are the hopping matrix elements between the extended and the localized states. For simplicity, we assume that

$$V_{ikm}=B_{km}\phi^i(s), \tag{8}$$

where we have used the observation[5] [see Eq. (1)] that V_{ikm} is approximately proportional to $\phi^i(s)$, and B_{km} is the constant of proportionality. U_{ij} are the Couloumb integrals between the localized states $U_{ij}\sim F^0(ii,jj)$, where

$$F^k(ij,kl)=e^2\int_0^\infty r^2dr\int_0^\infty(r')^2dr'\frac{r_<^k}{r_>^{k+1}}\phi_i(r)\phi_j(r)\phi_k(r')\phi_l(r'), \tag{9}$$

and $r_>$ ($r_<$) is the larger (smaller) of r and r'. Since ϕ_0 and ϕ_1 are orthogonal, the integrals of the type $F^0(ii,jj)$ are normally the largest ones. We have also included $\tilde{U}\sim F^0(ij,jj)$, where for simplicity we have assumed that $F^0(01,11)\approx F^0(01,00)$. The corresponding terms in (6) are particularly interesting, since they will allow ϕ_0 and ϕ_1 to mix in a way which is coupled to the number of localized electrons. Because of the factor $\tilde{n}_0+\tilde{n}_1-1$ in the last term, there is no mixing of $|\phi^0\rangle$ and $|\phi^1\rangle$ for configurations with n_l^0 localized electrons. This is the desired result, since $|\phi^0\rangle$ was constructed to be the solution of the radial Schrödinger equation for n_l^0 localized electrons. The Coulomb matrix elements of the type $F^0(01,01)$ are neglected, since we expect these to give smaller contributions than terms involving $F^0(01,00)$. We have also neglected terms containing F^k, $k=2,4$, which give multiplet effects, but are not of any particular interest for the issues discussed here. In the actual calculation of U_{ij} one has to take into account that there are strong renormalization effects.[9,10,5] This has already been included in the last term, by using the result (5) for $\tilde{U}$.

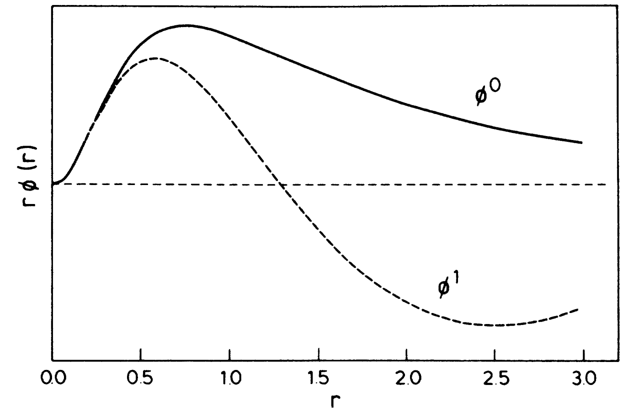

FIG. 1. The orbitals $\phi_{3d}^0(r)$ and $\phi_{3d}^1(r)$ for Mn in CdTe. We used the configuration $3d^5$ and the Wigner-Seitz radius $s=3.015$ a.u. and all the core levels were filled.

To obtain the model (6) we have made several simplifications. It still includes, however, the strong dependence of the radial extent of the localized orbital on the occupancy of this orbital, which is observed in *ab initio* calculations (see Table I), and which is the issue of this paper. To see this, we calculate the localized orbital for the occupancy n_l in the atomic limit ($V_{ikm}\equiv0$), using the Hartree-Fock approximation and perturbation theory

$$|\phi_l(n_l)\rangle=|\phi^0\rangle-\tilde{U}\frac{(n_l-n_l^0)}{\varepsilon_1-\varepsilon_0}|\phi^1\rangle, \tag{10}$$

where we have neglected the difference between U_{00} and U_{01}. This difference should not be very important, since $\varepsilon_1-\varepsilon_0=2.13$ Ry for Mn, while $\langle\phi^0|v^1|\phi^0\rangle-\langle\phi^1|v^1|\phi^1\rangle$

$=0.13$ Ry. For $n_l=6$ and $n_l^0=5$ the numerical coefficient of ϕ^1 is -0.08. From Fig. 1, we deduce $\phi^1(s)/\phi^0(s) \approx -3$, and from Table I we obtain $\tilde{\Delta}=0.0085$ for $n_{3d}=5$. We then predict $\tilde{\Delta}=(1+0.08\times 3)^2 0.0085 = 0.013$ [see Eq. (1)] for $n_{3d}=6$ in agreement with the full calculations, illustrating that the model (6) properly describes the radial relaxation of the localized orbital. This calculation also illustrates the validity of perturbation theory, which follows both from the relatively large energy separation of ϕ^0 and ϕ^1 and from the relatively small matrix element $\tilde{U}$. Both these results are consequences of the fact that ϕ^0 and ϕ^1 by construction are orthogonal. This reduces the matrix element $\tilde{U}$, since v^1 has a rather smooth variation. It further forces ϕ^1 to have one node more than ϕ^0 (see Fig. 1), which leads to a rather high energy. We expect this to be true also for other systems.

We now discuss how the model (6) can be approximately mapped back onto the normal Anderson model, by using the observation that the state $|\phi^1\rangle$ is much higher in energy than the state $|\phi^0\rangle$ (about 2 Ry = 27 eV for Mn), and that $|\phi^1\rangle$ is only weakly mixed into low-lying states. Assume we have a state $|\mu,n_l\rangle$, built up from n_l electrons in states $\{|0m\sigma\rangle\}$ of the type $|\phi^0\rangle$, and some combination of extended states $\{|k\sigma\rangle\}$. These kind of states span the whole space of states for the normal Anderson model. From one of these states we can construct a number of states $|\mu,n_l,\alpha\rangle$, by transferring zero, one or several localized electrons from states $|0m\sigma\rangle$ to states $|1m\sigma\rangle$. The space $\{|\mu,n_l,\alpha\rangle,\ \mu=1,2,\ldots\ n_l=0,1,\ldots\ \alpha=1,2,\ldots\}$ spans the two-orbital model above. For the space $\{|\mu n_l,\alpha\rangle, \alpha=1,2\ldots\}$ generated from one state $|\mu,n_l\rangle$, we diagonalize the Hamiltonian (6). All the new states, except possibly one, are high in energy. Thus, we only keep the lowest state in each space, which allows us to make a one to one mapping back onto the normal Anderson model. By calculating the hopping matrix elements between the states which are kept, we obtain a prescription for how to calculate the matrix elements in the Anderson model.

Using the first-order perturbation theory, we obtain

$$|\tilde{\mu},n_l\rangle = |\mu,n_l\rangle - \sum_{m,\sigma} \tilde{U}\frac{n_l-n_l^0}{\varepsilon_1-\varepsilon_0}\psi^\dagger_{1m\sigma}\psi_{0m\sigma}|\mu,n_l\rangle\,, \qquad (11)$$

where we have neglected the differences between the U_{ij} in the denominator. To first order in $\tilde{U}/(\varepsilon_1-\varepsilon_0)$ the state $|\tilde{\mu},n_l\rangle$ is normalized and its energy is equal to the energy of $|\mu,n_l\rangle$. We now calculate the hopping matrix element between two states with different number of localized electrons

$$\langle\tilde{\mu},n_l|H|\tilde{\nu},n_l-1\rangle = \left[1-\tilde{U}\frac{\phi^1(s)}{\phi^0(s)}\frac{n_l-n_l^0}{\varepsilon_1-\varepsilon_0}\right]\langle\mu,n_l|H|\nu,n_l-1\rangle\,, \qquad (12)$$

which is correct to first order. From (10) and to the accuracy we are working with here, it then follows that

$$\langle\tilde{\mu},n_l|H|\tilde{\nu},n_l-1\rangle = \frac{\phi_l(s,n_l)}{\phi_l(s,n_l^0)}\langle\mu,n_l|H|\nu,n_l-1\rangle\,. \qquad (13)$$

To obtain the matrix elements between states with n_l and n_l-1 localized electrons, the calculation of $\tilde{\Delta}$ in (1) should therefore be performed for $n_l^0=n_l$, i.e., for the larger of the two occupation numbers. A simple way of seeing this is to note that $|\tilde{\mu},n_l^0\rangle$ is equal to $|\mu,n_l^0\rangle$, while $|\tilde{\mu},n_l^0-1\rangle$ takes the form of (11). The Hamiltonian (6) connects the first term in the expansion of $|\tilde{\mu},n_l^0-1\rangle$ to $|\mu,n_l^0\rangle$, but not the second term, and only V_{0km} enters the calculation.

We can now write down the proper hopping term, H_1, in the Anderson Hamiltonian

$$H_1 = \sum_{k,m,\sigma}[V_{km}(\hat{n})\psi^\dagger_{m\sigma}\psi_{k\sigma}+\psi^\dagger_{k\sigma}\psi_{m\sigma}V_{km}(\hat{n})]\,, \qquad (14)$$

where $\hat{n}=\sum_{m,\sigma}n_{m\sigma}$, and $V_{km}(n_l)$ has been calculated for n_l localized electrons. The rest of the Anderson model remains unchanged. The term (14) can be included in calculations[2] for the Anderson model without any complications. In calculations using the Anderson model it is often assumed that only two configurations are important. The Hamiltonian (14) then introduces no additional parameter compared with the normal Anderson model, but it gives a prescription for how to calculate the hopping matrix element.

For Ce compounds the f^0 and f^1 configurations are important for the thermodynamic properties and the valence photoemission spectrum. The corresponding matrix elements should then be calculated for $n_{4f}=1$. In particular, for valence photoemission, the f^2 configurations are, however, of importance as well, which also leads to matrix elements calculated for $n_{4f}=2$. In the core-level photoemission (XPS) spectrum and in the $3d$ x-ray absorption (XAS) spectrum the hopping matrix elements in particular influence the peaks related to f^1 and f^2 states. This influence is both via the ground-state and final-state properties. In the final states, the matrix elements, most important for the weights of the f^1 and f^2 peaks, should be calculated for $n_{4f}=2$ in the presence of a core hole. In the XPS (XAS) the weight of the f^2 peak also depends on the f^2 (f^1) weight in the initial state, which is related to $\tilde{\Delta}$ calculated for $n_{4f}=2$ ($n_{4f}=1$). The net result of these effects is that an effective matrix element $|V|^2$ (used in a Hamiltonian without configuration dependence) appears somewhat larger ($\sim$20%) in core-level XPS and smaller in $3d$ XAS compared with the $|V|^2$ calculated for $n_{4f}=1$ in the absence of a core hole. In core-level XPS, multiplet effects have usually been neglected, which should tend to reduce the apparent size of $|V|^2$. In the bremsstrahlung isochromat spectroscopy (BIS), we are often interested in the relative weights of the f^1 and f^2 peaks. In the final-state calculation, the corresponding important matrix elements should be obtained for $n_{4f}=2$, while the important ground-state matrix elements should be obtained for $n_{4f}=1$. An effective $|V|^2$ should then appear larger than the $|V|^2$ calculated for $n_{4f}=1$. Thus we expect an effective $|V|^2$ to be similar for the thermodyanic properties and the valence and core-level photoemission spectra, while it should be larger for BIS and smaller for $3d$ XAS spectra.

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