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LETTER TO THE EDITOR

A modified form for the real-space embedding potential

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Abstract. An alternative form for the real-space embedding potential of Inglesfield is derived. The new form does not involve inverting a Green function over a surface, but it does involve normal derivative terms. The relationship to the embedding potential for a system described by a discrete basis set is clarified.

Suppose we wish to find the eigenstates ψ_E of the Schrödinger equation with energy E, but to restrict our calculation to some subdomain of space (region 1) while implicitly accounting for the presence of the rest. This type of situation arises in electronic structure calculations at point, line and planar defects in solids where one wishes to account for the presence of the bulk; the subdomain 1 is then the region of space immediately surrounding the defect. The most usual approach to such a problem involves the use of scattering theory; alternatives do however exist in the form of Green function matching techniques (Inglesfield 1970, Heine 1980) or embedding theories (Inglesfield 1981, Baraff and Schlüter 1986, Fisher 1988, Inglesfield and Benesh 1988). The embedding theories can be formulated either in real space or in an arbitrary set of basis functions and rely on adding an effective energy-dependent potential, usually known as the embedding potential, to the Hamiltonian at the boundary between region 1 and region 2. The embedding potential has the effect of constraining the wave-function to satisfy the correct boundary condition at the surface.

Forms are available for the embedding potential which, broadly speaking, involve inverting a Green function either over the whole of region 1 or over the surface between the regions. This inversion can be difficult to perform, especially in defect problems where the surface may have an irregular shape and a convenient set of orthogonal functions upon it may not be available. In this letter we show how it is possible to write the embedding potential in real space particularly simply, in a form that does not involve any inversions, in terms of the bulk Green function that vanishes on the surface. This is interesting because it mirrors the structure of the simplest possible forms for the embedding potential in a discrete basis set, which have been known for over forty years (Feshbach 1948). Finally we shall show how the new form may be used to find the embedding potential for all values of the angular momentum for a spherical embedding surface where the potential in the external region 2 is uniformly zero. The known solution for the s-wave case $l = 0$ is recovered.

First we consider the alternative form for the embedding potential in real space. Inglesfield (1981) has shown that the boundary condition on ψ_E over the surface S separating region 1 from the remaining region 2 can be expressed (in atomic units

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where $\hbar = m_e = 1$) in the form

$$\frac{\partial \psi_E(\boldsymbol{r})}{\partial n} = 2\int_S \mathrm{d}^2\boldsymbol{r}_1\, \Sigma_E(\boldsymbol{r},\boldsymbol{r}_1)\psi_E(\boldsymbol{r}_1) \tag{1}$$

where $\boldsymbol{r}$ is supposed to lie on the surface S, the integral runs over the surface S, $\partial/\partial n$ denotes the derivative normal to S and Σ_E is a non-local energy-dependent operator that is defined on S and known as the embedding potential.

Inglesfield (1981) derives the following expression for the embedding potential:

$$\Sigma_E(\boldsymbol{r},\boldsymbol{r}_1) = \int_S \mathrm{d}^2\boldsymbol{r}_2\, G_E^{-1}(\boldsymbol{r}_2,\boldsymbol{r})\left(\delta^2(\boldsymbol{r}_1-\boldsymbol{r}_2) + \frac{1}{2}\frac{\partial}{\partial n_1}G_E(\boldsymbol{r}_1,\boldsymbol{r}_2)\right) \tag{2}$$

where G_E is any Green function for the Schrödinger equation in region 2, i.e. satisfying

$$(-\tfrac{1}{2}\nabla_1^2 + V(\boldsymbol{r}_1) - E)G_E(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\delta(\boldsymbol{r}_1-\boldsymbol{r}_2) \tag{3}$$

when $\boldsymbol{r}_1, \boldsymbol{r}_2$ lie in region 2 and G_E^{-1} is the inverse of this quantity on the surface S, i.e. the operator which satisfies

$$\int_S \mathrm{d}^2\boldsymbol{r}_2\, G_E(\boldsymbol{r}_1,\boldsymbol{r}_2)G_E^{-1}(\boldsymbol{r}_2,\boldsymbol{r}_3) = \delta^2(\boldsymbol{r}_1-\boldsymbol{r}_3)\,. \tag{4}$$

Equation (2) becomes especially simple if the Green function is chosen to satisfy the von Neumann boundary condition that its normal derivative vanishes on S; the embedding potential then becomes simply the surface inverse G_E^{-1}.

We shall now show that another simple expression for the embedding potential in terms of the Green function can be obtained if the latter is chosen to satisfy, not a von Neumann boundary condition, but the Dirichlet boundary condition

$$G_E(\boldsymbol{r}_1,\boldsymbol{r}_2) = 0 \tag{5}$$

whenever $\boldsymbol{r}_1$ or $\boldsymbol{r}_2$ lies on S. We begin by multiplying the Schrödinger equation for $\psi_E(\boldsymbol{r}_1)$ by $G_E(\boldsymbol{r}_1,\boldsymbol{r}_2)$ and equation (3) by $\psi(\boldsymbol{r}_1)$, integrating the coordinate $\boldsymbol{r}_1$ over region 2, subtracting and using Green's theorem with the convention that normal derivatives are defined in the direction passing from region 1 into region 2 to obtain:

$$\psi_E(\boldsymbol{r}_2) = -\frac{1}{2}\int_S \mathrm{d}^2\boldsymbol{r}_1\left(\frac{\partial}{\partial n_1}G_E(\boldsymbol{r}_1,\boldsymbol{r}_2)\right)\psi_E(\boldsymbol{r}_1)\,. \tag{6}$$

Taking the normal derivative with respect to the coordinate $\boldsymbol{r}_2$ we find

$$\frac{\partial}{\partial n_2}\psi_E(\boldsymbol{r}_2) = -\frac{1}{2}\int_S \mathrm{d}^2\boldsymbol{r}_1\left(\frac{\partial^2}{\partial n_1 \partial n_2}G_E(\boldsymbol{r}_1,\boldsymbol{r}_2)\right)\psi_E(\boldsymbol{r}_1)\,. \tag{7}$$

Comparing with Equation (1) we find that the embedding potential is given by

$$\Sigma_E(\boldsymbol{r}_2,\boldsymbol{r}_1) = -\frac{1}{4}\frac{\partial^2}{\partial n_1 \partial n_2}G_E(\boldsymbol{r}_1,\boldsymbol{r}_2)\,. \tag{8}$$

This is our principal result. Its significance is twofold. First, it permits one to obtain the embedding potential without the need to perform a surface inversion; this may be advantageous if the surface S is a complicated shape so that it is not convenient to find an orthogonal set of functions upon it in which to expand G_E. Secondly, it provides an immediate link with the corresponding theory of embedding for a discrete basis set.

We next consider the connection with embedding in a discrete basis set. If we consider a problem described, not in terms of a Hamiltonian in real space but in terms of a Hamiltonian matrix in some basis set, it is still possible to use very similar embedding techniques to reduce the problem to one involving just some part of the whole basis set. For example, the basis set might consist of localised atomic orbitals and we might wish to work only with the states immediately surrounding some defect (Feshbach 1948, Pryce 1950, Löwdin 1951, Baraff and Schlüter 1986, Fisher 1988). If the matrix $\mathbf{Q}$ is defined as

$$\mathbf{Q} = E\mathbf{I} - \mathbf{H} \tag{9}$$

and the basis is partitioned into two subsets 1 and 2, then it is easy to show that the wave function projected onto subset 1, ψ^1, satisfies the equation

$$(\mathbf{Q}_{11} - \Sigma_{11})\psi^1 = 0 \tag{10}$$

where the embedding potential for the discrete basis set is

$$\Sigma_{11} = \mathbf{Q}_{12}(\mathbf{Q}_{22})^{-1}\mathbf{Q}_{21}\,. \tag{11}$$

The analogy between (8) and (11) straightforward; the inverse of the matrix $\mathbf{Q}_{22}$ is simply the Green function for region 2 when it is decoupled from region 1, while $\mathbf{Q}_{12}$ and $\mathbf{Q}_{21}$ are analogous to the normal derivative terms which, for a local potential, are the only parts of the Hamiltonian which are not diagonal in the real-space position representation.

Finally, we discuss as an example the embedding potential for the case treated by Inglesfield (1970, 1981) in which the applied potential is uniformly zero outside a sphere of radius r_s. We take this sphere as the surface S; the eigenstates in region 2 which vanish on S with energy $E = k^2/2$ are

$$\psi_{lmk}(r,\theta,\phi) = Y_{lm}(\theta,\phi)R_l(kr) \tag{12}$$

where Y_{lm} is a spherical harmonic and the radial function R_l is given by

$$R_l(kr) = \left(h_l^{(1)}(kr) + A_l(k)h_l^{(2)}(kr)\right) \tag{13}$$

with

$$A_l(k) = -\frac{h_l^{(1)}(kr_s)}{h_l^{(2)}(kr_s)}\,. \tag{14}$$

Here $h_l^{(1)}$ and $h_l^{(2)}$ are the spherical Hankel functions (Abramowitz and Stegun 1965). The retarded Green function which obeys the Dirichlet boundary condition (5) can be written as a sum over these eigenstates

$$G_E(\boldsymbol{r}_1,\boldsymbol{r}_2) = \lim_{\eta\to 0+}\sum_{lm}\int_0^\infty \frac{\psi_{lmk}(\boldsymbol{r}_1)\psi^*_{lmk}(\boldsymbol{r}_2)}{2\pi(E - \frac{1}{2}k^2 + \mathrm{i}\eta)}\,k^2\mathrm{d}k \tag{15}$$

and the integral can be evaluated by contour integration. If we write the result in the form

$$G_E(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)=\sum_{lm}Y_{lm}(\theta_1,\phi_1)Y^*_{lm}(\theta_2,\phi_2)G_l(E,r_1,r_2) \tag{16}$$

then

$$G_l(E,r_1,r_2)=-ikh_l^{(1)}(kr_>)\big(h_l^{(2)}(kr_<)+A_l^*(k)h_l^{(1)}(kr_<)\big) \tag{17}$$

for $E>0$, where $r_>$ and $r_<$ are respectively the larger and the smaller of r_1 and r_2. From equation (8), the coefficients in the corresponding expansion of the embedding potential are therefore

$$\Sigma_l(E)=-\frac{ik^3}{4}h_l^{(1)\prime}(kr_s)\big(h_l^{(2)\prime}(kr_s)+A_l^*(k)h_l^{(1)\prime}(kr_s)\big) \tag{18}$$

For the special case $l=0$ we recover Inglesfield's result

$$\Sigma_0(E)=-\frac{1}{2r_s^3}(1-ikr_s)\,. \tag{19}$$

To conclude, we have derived a new expression for the embedding potential which clarifies the relationship with the corresponding form for a discrete basis set. The new expression does not require one to perform any surface inversion to calculate the embedding potential. We have shown how the new formula reproduces the known results for a spherically symmetric embedding surface surrounded by an infinite region of zero potential. It should be stressed, however, that the procedure relies on one's ability to construct a Green function with the required Dirichlet boundary condition (5); the difficulty of finding the analogous quantity $\mathbf{Q}_{22}^{-1}$ in a discrete basis set has prevented the use of equation (11) as a practical expression for the embedding potential. It may be, therefore, that the chief value of the present work is conceptual, in that it draws once again an analogy between real space and other possible basis sets.

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