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## LETTER TO THE EDITOR

# A non-local Hartree–Fock approach to embedding

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**Abstract.** A new non-local Hartree–Fock approach to the embedding of a single impurity (atom, ion or molecule) into a solid is proposed. The method, which is based on both a coupled Hartree–Fock calculational scheme and the Green function embedding method of Inglesfield, aims at calculating lifetimes of the electronic states of the embedded impurity, either in its ground or an excited state. As an example, we present an application of this method to the embedding of a Li and a He atom into a metallic jellium.

Recently, Andriotis and Nicolaides have developed [1] a non-local Hartree–Fock (HF) theory in order to describe the interaction of an atom (or ion) with a metal surface. The method is based on the coupled Hartree–Fock (CHF) calculational scheme [2] and its application is based on the assumptions that (i) the adatom/adion exhibits atomic-like behaviour, and (ii) the disturbance that the adatom introduces into the substrate can be described by an orthogonalisation process by which the single-electron states,  $\Psi_k(\mathbf{r})$ , of the metal substrate become orthogonal to the orbital states,  $\Psi_a(\mathbf{r})$ , of the adatom.

These assumptions are fulfilled in the case of embedding atoms/ions with closed electronic shells into a metal. Of particular interest is the application of the CHF approach to the interaction of noble-gas atoms with metal surfaces [1, 3]. On the other hand, atoms with open outer electronic shells, when embedded in metals, may have their outer electrons (mainly) strongly mixed with the metallic electron orbitals [4, 5]. As a result, the energy levels of the embedded atom/ion (to be called the impurity) evolve into resonances exhibiting a broadening that is associated with a measurable line-width. The development of such resonances is similar to the autoionisation process and results from the ‘configuration interaction’ which mixes states of the same energy but of different configurations [4]. One way to obtain the energies ( $E$ ) and the widths ( $\Gamma$ ) of resonance states is dictated by the so-called ‘complex coordinate method’ (CCM) [6].

According to the CCM, the time-independent single-electron Hamiltonian is analytically continued in the complex energy plane and its complex eigenvalues,  $e$ , are found. The energy position of the resonance is associated with the real part of  $e$  while the line-width is associated with the imaginary part, ( $e = E - i\Gamma/2$ ). In an analogous way to the CCM, in the present work we claim that the mixing of the continuum metal states with the discrete impurity states is associated with a complex crystal potential which is appropriately calculated. Consequently, the position and the width of the impurity resonances may be found from the eigenvalues of the Hamiltonian of the system which is analytically continued in the complex energy plane.

The idea for such an approach originated following the embedding approach of Inglesfield [7] who introduced a complex embedding potential using the Green function of the impurity-free substrate. According to Inglesfield's embedding technique, a limited region of space, to be called the 'impurity region', is considered within the substrate containing the impurity and separated by a surface  $\mathcal{S}$  from the rest of the substrate. In the impurity region the wavefunctions satisfy the Schrödinger equation

$$-\frac{1}{2}\nabla^2\Psi_a + (V(\mathbf{r}) + V_{\text{ext}}(\varepsilon_{\text{in}}, E; \mathbf{r}))\Psi_a = E\Psi_a \quad (1)$$

where  $V(\mathbf{r})$  is the single-electron potential in the impurity region and  $V_{\text{ext}}(\varepsilon_{\text{in}}, E; \mathbf{r})$  is defined on the surface  $\mathcal{S}$  in terms of the embedding potential  $G_0^{-1}(\mathbf{r}_s, \mathbf{r}'_s; \varepsilon_{\text{in}})$  at input energy  $\varepsilon_{\text{in}}$  by the equation [7]

$$V_{\text{ext}}(\varepsilon_{\text{in}}, E; \mathbf{r})\Psi_a(\mathbf{r}) = \delta(\mathbf{n} - \mathbf{n}_s) \left[ \frac{1}{2} \frac{\partial\Psi_a}{\partial n_s} + \int_{\mathcal{S}} d\mathbf{r}'_s \left( G_0^{-1}(\mathbf{r}_s, \mathbf{r}'_s; \varepsilon_{\text{in}}) + (E - \varepsilon_{\text{in}}) \frac{\partial G_0^{-1}}{\partial \varepsilon_{\text{in}}} \right) \Psi_a(\mathbf{r}'_s) \right] \quad (2)$$

where  $\mathbf{r}_s$  is a point on  $\mathcal{S}$  and  $\mathbf{n}(\mathbf{n}_s)$  the component of  $\mathbf{r}(\mathbf{r}_s)$  perpendicular to  $\mathcal{S}$ .

The introduction of the potential  $V_{\text{ext}}$  into (1) is necessary in order to have  $\Psi_a(\mathbf{r})$  correctly matched on  $\mathcal{S}$  with the wavefunctions outside the impurity region. As is evident from (2),  $V_{\text{ext}}$  is energy dependent. The appropriate input energy [7]  $\varepsilon_{\text{in}}$  is the one for which  $\varepsilon_{\text{in}} = E$ .

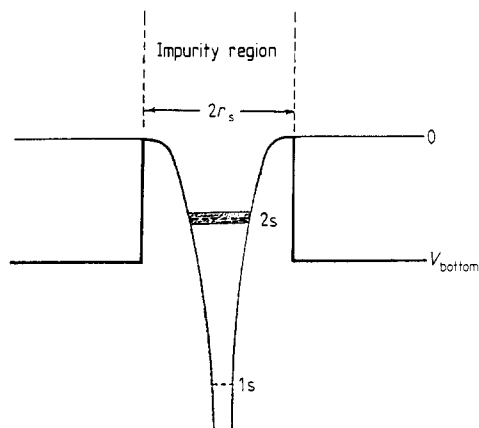
The CCM ensures that we can solve (1) by expanding  $\Psi_a(\mathbf{r})$  in square integrable functions. As such we use the Gaussian-type orbitals (GTOs) and we solve (1) as we did in the case of a real  $V_{\text{ext}}$  potential using the CHF calculational scheme [1]. The major differences between the present case and the CHF case is the energy dependence of  $V_{\text{ext}}$  and the fact that the one- and two-electron integrals are evaluated over the impurity region [7]. On the other hand, the functional dependence of  $V_{\text{ext}}$  on the energy will dictate the numerical approach one can follow to obtain the eigenvalues of (1). For the general purposes of the present work, we have developed a computer code that is based on the algorithm of the analytic HF method [8], appropriately modified for the case of complex functions.

As a first application of the present method, we have chosen the problem of embedding a He or a Li atom into a metallic jellium. The physical picture of our problem is depicted in figure 1. In the spherical impurity region defined by the radius  $r_s$ , the potential is taken to be the (non-local) HF potential of the impurity atom. Outside the impurity region the potential is that of a metallic jellium and is specified by the value of the bottom of its conduction band,  $V_{\text{bottom}}$ . For this model, the embedding potential is taken, according to Inglesfield [7], from the s-component of the free-electron Green function, i.e.

$$G_0^{-1}(\mathbf{r}_s, \mathbf{r}'_s; \varepsilon_{\text{in}}) = [1 + r_s \sqrt{2(V_{\text{bottom}} - \varepsilon_{\text{in}})}] / 8\pi r_s^3 \quad (3)$$

where the energy  $\varepsilon_{\text{in}}$  is measured with respect to the empty space (vacuum).

In order to incorporate Inglesfield's approach into our non-local HF calculational scheme (as dictated by our CHF approach [1]), we consider (2) and (3) for  $\varepsilon_{\text{in}} = E$ . In the



**Figure 1.** Schematic representation of the single-electron potential for an impurity embedded in a metallic jellium.

case of s-type impurities, like the present one, after expanding  $\Psi_a(r)$  in GTOS, the combination of (1)–(3) leads to the following matrix problem:

$$(k^2 \mathbf{S} + \sqrt{2} k r_s \mathbf{R}^{(0)} + \mathbf{H}) \mathbf{y} = 0 \quad (4)$$

$$k^2 = V_{\text{bottom}} - E \quad (5)$$

where  $\mathbf{S}$  is the overlap matrix and the matrix elements of  $\mathbf{R}^{(0)}$  and  $\mathbf{H}$  are given by the expressions

$$H_{ij} = H_{ij}^{(0)} + R_{ij} - V_{\text{bottom}} S_{ij} \quad (6)$$

$$R_{ij} = (r_s - 2\beta_j r_s^3) R_{ij}^{(0)} \quad (7)$$

$$R_{ij}^{(0)} = (2^{5/2} / \pi^{1/2}) (\beta_i \beta_j)^{3/4} \exp[-(\beta_i + \beta_j) r_s^2]. \quad (8)$$

In the above expressions  $\beta_i$  are the exponents of the GTOS and  $H_{ij}^{(0)}$  is the HF Hamiltonian of the free impurity. Equation (4) can be solved, in general, by diagonalising the quadratic (in  $k$ ) matrix [9]. However, in the present case initial attempts indicated that a diagonalisation process cannot be applied for the solution of (4) because matrix  $\mathbf{R}^{(0)}$  has very few non-zero elements. For this reason we solved (4) iteratively starting with the zeroth-order equation

$$(k^2 \mathbf{S} + \mathbf{H}) \mathbf{y} = 0 \quad (9)$$

which can be solved by ordinary diagonalisation. The whole iterative procedure used for solving (4) is repeated until (4) attains a self-consistent solution with respect to the mean value of the Hamiltonian given by (6) according to the algorithm of the analytic HF method [8].

In tables 1 and 2 we present results obtained according to the present method for the total HF energies and orbital energies for a He and a Li atom, respectively, embedded in jellium of given parameters  $r_s$  and  $V_{\text{bottom}}$ . The total HF energies refer to the average value of  $\mathbf{H}$  given by (6). This is a good approximation as long as  $\mathbf{R}^{(0)}$  has elements whose absolute values are much smaller than unity. In the case of very strong impurity–metal interaction, i.e. in the case where the elements of  $\mathbf{R}^{(0)}$  are large, the present procedure must be changed not only in the scheme of the iterative solution of (4) but also in the expression of the total HF energy. Calculations along these lines are in progress and will

**Table 1.** Results for the total Hartree–Fock energy and the 1s electron orbital energy (all in au) for a He atom embedded into a metallic jellium for  $r_s = 4.0$  au and various depths.

$V_{\text{bottom}}$	$\epsilon_{1s}$	$E_{\text{HF}}$
-0.25	(-0.92179, 0.00000)	(-2.864644310, 0.0)†
-0.75	(-0.92299, 0.00000)	(-2.865211961, 0.0)†
-1.10	(-0.92494, -0.00060)	(-2.865761240, $1.081 \times 10^{-5}$ )†
-1.40	(-0.92509, -0.00098)	(-2.865685601, $1.772 \times 10^{-5}$ )†
Free He atom	-0.9179	-2.861491091

† Expected value of the Hamiltonian given by (6).

**Table 2.** Results for the total Hartree–Fock energy and the 1s and 2s electron orbital energies (all in au) of a Li atom embedded into a metallic jellium for  $V_{\text{bottom}} = -0.40$  au and various ranges.

$r_s$	$\epsilon_{1s}$	$\epsilon_{2s}$	$E_{\text{HF}}$
4.0	(-2.43512, -0.00069)	(-0.20715, -0.07823)†	
7.0	(-2.51583, 0.00000)	(-0.21156, -0.03118)	(-7.453108229, $2.39863 \times 10^{-3}$ )‡
10.0	(-2.48195, 0.00000)	(-0.19779, -0.00107)	(-7.430944491, $2.07573 \times 10^{-5}$ )‡
15.0	(-2.47535, 0.00000)	(-0.19622, 0.00000)	(-7.422934766, $2.56 \times 10^{-14}$ )‡
Free Li atom	-2.47533	-0.19622	-7.429346501

† Not converged in  $E_{\text{HF}}$ ; see the text.

‡ Expected value of the Hamiltonian given by (6).

be reported elsewhere. In the case of strong impurity–metal interaction (i.e. large value of  $V_{\text{bottom}}$  or/and small values of  $r_s$ ) within the present method, we usually observe a poor convergence towards self-consistency. In particular, we observe an oscillation in the eigenvalues which, however, is limited to the fifth or higher significant figure. To such a solution the result for a jellium of  $r_s = 4.0$  au is referred to in table 2.

As expected, our results indicate that the eigenstates that have eigen-energies above the bottom of the conduction band of the host metal exhibit a broadening that depends on the strength of the embedding potential and the distance of the energy level from the bottom of the conduction band. This is more pronounced in the embedding of Li, as this impurity has an open electron shell. The calculated line-widths for the 2s state of Li appear quite large even for moderate impurity–host interactions.

At this stage it is worth emphasising that the present method allows us to work separately on the impurity and the host metal. Thus we can concentrate on the impurity (atom or cluster) and apply the various calculational schemes of atomic (or molecular) physics to the embedded impurity. The present calculation refers only to the HF level of approximation with respect to the impurity. However, as this method is not restricted to the study of the ground state of the impurity, one can attempt to generalise it to a desirable CI level. The only drawback is that the host metal is bound to the existing calculational schemes for the band structure which are limited to the local density approximation (LDA). Nevertheless when a realistic Green function for the host is used, the present method provides one with the possibility of combining existing highly

accurate techniques of atomic physics with those of solid state physics that can account for band structure effects.

At the completion of this work, I became aware of the work of Nordlander and Tully [10] who reported calculations based on the CCM [6] for lifetimes and energy shifts of hydrogen-atom excited states in the vicinity of a jellium surface. Although their approach is completely different to ours, the principle of the analytic continuation of the Hamiltonian in the complex plane is common to the two cases. The basic qualitative difference between the two methods is that in our case we have anticipated that the complex embedded potential, and therefore the Hamiltonian that we have employed, have the analytic properties that are required by the CCM method [6]. This assumption is widely used in atomic calculations when potentials other than the dilatation analytic ones are used [11]. Within these assumptions, it is worth noticing that the present method can equally well be used for accurate calculations of energy shifts and lifetimes of excited states of either free or embedded/physisorbed atoms.

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