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LETTER TO THE EDITOR

The complex-Hamiltonian approach

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Abstract. It is pointed out that when a complex-Hamiltonian technique is employed for solving Schrödinger's equation either in solids or atoms, the location of the resonances cannot be accurately determined by specifying the real energies at which the imaginary part of the corresponding Green's function exhibits resonance peaks. Instead of spanning the real energy axis to locate the peaks of the electron DOS, it is more accurate to solve the complex Hamiltonian in the entire complex energy plane. In particular, it is demonstrated that the locations of the resonances of an embedded atom which are obtained by a direct diagonalization of the complex Hamiltonian in the complex energy plane do not coincide in general with the peaks of the electron DOS obtained from a Green's function approach.

Various theoretical approaches to many-particle systems, such as metal surfaces, chemisorbed systems, impurity systems, alloys etc., lead to efficient calculational schemes which have one common characteristic: they transform the problem under consideration into an equivalent one in which a complex, energy-dependent Hamiltonian $H(\mathbf{r}; E)$ (which in general is non-Hermitian) replaces the original real, Hermitian (single-electron) Hamiltonian of the system under consideration. Among these calculational schemes we mention the complex coordinate method (CCM) [1], the sub-space Hamiltonian method [2], the embedding scheme of Inglesfield [3] and the coherent potential approximation (CPA) [4].

In order to extend the computational techniques which are used to calculate bound states of atoms and molecules into the case of resonances (continuum or scattering states) the CCM employs an analytical continuation of the Hamiltonian in the complex energy plane. On the other hand, the sub-space Hamiltonian method and the embedding scheme of Inglesfield offer the advantage of replacing the effect of a surrounding host environment on a small sub-space of the system of interest by introducing an energy-dependent Hamiltonian which is complex and non-Hermitian in general. Finally, the CPA aims at the calculation of a complex, energy-dependent self-energy which results in a complex, energy-dependent Hamiltonian.

The information which is obtained from the solution of the complex Hamiltonian is usually the bound and resonance states of the system and the associated electron density of states (DOS). The calculational techniques which are commonly used to solve the complex Hamiltonian that we mentioned above depend on the quantity one is interested in and go along two major avenues of calculation. According to the first one the complex Hamiltonian is solved (diagonalized) in the complex energy plane

and its complex eigenvalues are obtained

$$H(\mathbf{r}; E)\Psi_i(\mathbf{r}; E) = E_i(E)\Psi_i(\mathbf{r}; E). \quad (1)$$

As Allen and Menon indicate [2], the energies at which $E_i(E) = E$ specify the bound states of the Hamiltonian if E is real and specify its resonant states if E is complex. It is only for very narrow resonances that their location may be approximately determined by the approximate relation [2]

$$\text{Re } E_i(E) = E. \quad (2)$$

This can be verified [2] by writing the spectral representation of the Green's function $G(\mathbf{r}, \mathbf{r}'; E)$ which corresponds to the complex, energy-dependent Hamiltonian $H(\mathbf{r}; E)$, i.e.

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_i \frac{\Psi_i(\mathbf{r}; E)\Psi_i^\dagger(\mathbf{r}'; E)}{E - E_i(E)} \quad (3)$$

assuming that

$$\sum_i \Psi_i(\mathbf{r}; E)\Psi_i^\dagger(\mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}'). \quad (4)$$

According to the second calculational approach, the energy-dependent Hamiltonian is used to obtain the corresponding Green's function, $G(E)$, of the system from which the electron DOS, $\rho(E)$ is obtained. The locations of the peaks of the electron DOS as one spans the energy along the *real* energy axis are associated with the energies of the resonances of the Hamiltonian.

In view of equation (2) one realizes that the second calculational approach is only approximately valid and not equivalent with the first calculational scheme in general. It is this, the problem of equivalence between the two calculational schemes discussed above, that we would like to address in the present letter.

It has been anticipated that both calculational approaches to the solution of the complex Hamiltonian problem are equivalent although according to equations (1)–(4) one could argue that these two methods are not equivalent in general because the Green's function approach restricts itself in a spanning along the real energy axis while the direct diagonalization of the complex Hamiltonian searches for solutions in the *whole complex energy plane*. On the basis of the classical theory of resonances, this argument sounds misleading as one expects *any* resonance to be exhibited as a peak in the electron DOS along the real energy axis. However, such a statement refers to real Hamiltonians and it is different from the problem which I would like to address in the present letter which refers to a complex Hamiltonian containing a potential which depends on the (complex) energy. In the latter case, it will be shown that the two approaches mentioned above are not equivalent in general as equations (1)–(4) imply. This problem seems to be the cost that is paid when one transforms an infinite-space problem into a problem extended over a finite volume, or when calculational techniques suitable for bound states are applied in order to calculate scattering or resonance states. Putting the problem in another way we can say that we question here how accurately the formal equation

$$\rho(E) = -(1/\pi) \text{Im Tr } \mathbf{G}(E) \quad (5)$$

traces the poles of $\mathbf{G}(E)$ when E is restricted on the real axis even though $\mathbf{G}(E)$ is associated with a complex Hamiltonian.

In the case of the CPA, one calculates corrections to the eigenvalues (i.e., the coherent potentials or self-energies) and thus the CPA is inherently associated with a solution over the whole complex energy plane. In this case no problem of equivalence appears and the CPA is a valid solution to the associated complex-Hamiltonian problem. Thus, the problem of equivalence which is presently addressed refers to the comparison between the methods which solve the complex Hamiltonian in the *whole* complex plane, as the CCM does, and those which rely on the calculation of the electron DOS by spanning the *real* energy axis although a complex energy-dependent potential is present in the Hamiltonian.

This problem of equivalence between the two methods of solving the complex Hamiltonian problem was checked by Inglesfield [3] in an effort to demonstrate the applicability of an efficient embedding scheme aimed at treating a wide class of impurity and surface problems. According to Inglesfield's results and within the anticipated accuracy, the equivalence of the two methods appeared to be satisfactory. However, a more careful and accurate reexamination of his results indicates that small discrepancies between the results of the two methods cannot be eliminated and therefore the two methods are not exactly equivalent. In particular, we observe that the peaks of the electron DOS of his example (figure 4 of [3]) are found at energies 1.70 and 6.5 au while the quoted results of a direct-diagonalization approach give eigenvalues with real part 1.3 and 6.2 au respectively. This observation made us reexamine the problem of equivalence with more elaborate calculations in the case of atomic resonances where the CCM has proved extremely efficient in locating the energies of atomic resonances by solving the Hamiltonian according to equations (1) and (2).

In the present letter, we report on results obtained by the two methods of solving the complex-Hamiltonian problem described above. In particular, we present results from the solution of a complex Hamiltonian, namely that of an atom embedded in a metal host, obtained by both an accurate direct-diagonalization method and the Green's function approach.

Our system of consideration refers to an atom embedded in a metal host, the latter approximated by the jellium model [5, 6]. Our method utilizes Inglesfield's embedding approach [3] and the coupled Hartree-Fock (CHF) scheme of Cohen and Roothaan [7, 8]. Inglesfield's scheme allows us to define an energy-dependent Hamiltonian term $V(\mathbf{r}; E)$ which reflects the effect of the metallic host on the embedded impurity. This term is added to the free-impurity atomic Hamiltonian which therefore becomes complex and energy dependent. The so-obtained Hamiltonian is subsequently solved within the CHF approximation which is based on a direct diagonalization of the complex Hamiltonian. The details of this method have been reported elsewhere, where results for embedded He, Li and excited Ar (KL $3p^5 4s^1$) atoms were given [5, 6].

The same embedded systems as the reported ones (He, Li, Ar) were also studied using the Green's function approach. In particular, at self-consistency of our Hartree-Fock solution we saved the Hartree-Fock Hamiltonian $H_{ij}(E)$ and the overlap matrix S_{ij} from which we obtained the Green's function, $G(\mathbf{r}, \mathbf{r}; E)$, and the electron DOS $\rho(E)$ according to Inglesfield's approach [3], i.e.

$$(\mathbf{H}^{(l)} - E\mathbf{S}^{(l)})\mathbf{G}^{(l)} = -\mathbf{I} \quad l = s, p \quad (6)$$

$$\rho^{(l)}(E) = (1/\pi) \text{Im Tr } \mathbf{G}^{(l)}(E) \quad l = s, p. \quad (7)$$

In figure 1 we give a representative example of the electron DOS obtained according to equations (6) and (7) for an excited argon atom embedded in a metallic jellium. As is apparent from the results in table 1, the location of the peak of the electron DOS does not coincide with the real part of the corresponding eigenvalue obtained by direct diagonalization. This discrepancy is exhibited in our results as far as the embedding potential $V(\mathbf{r}; E)$ is complex. When $V(\mathbf{r}; E)$ becomes real or sufficiently small, the two calculational schemes give results identical to those shown in table 1. In our calculations of the electron DOS according to equations (6) and (7) we had fixed the imaginary part of the energy to be $\text{Im } E = -0.0005$ (au) and our tolerance in locating the peak of the electron DOS is ± 0.0005 au.

Table 1.

Element	Radius of impurity region	Eigenvalue of outer electron ϵ		Location of electron DOS peak (equation (2))
		Re ϵ	Im ϵ	
Ar* (KL 3p ⁵ 4s)	5.0	-0.11572	-0.13821	-0.1830
	7.5	-0.17166	-0.04641	-0.1790
	10.0	-0.14995	-0.00638	-0.1500
Li (1s ² 2s)	3.0	-0.17187	-0.16058	-0.1685
	5.0	-0.22035	-0.07755	-0.2220
	7.0	-0.21202	-0.03168	-0.2090
	10.0	-0.19781	-0.00107	-0.1975

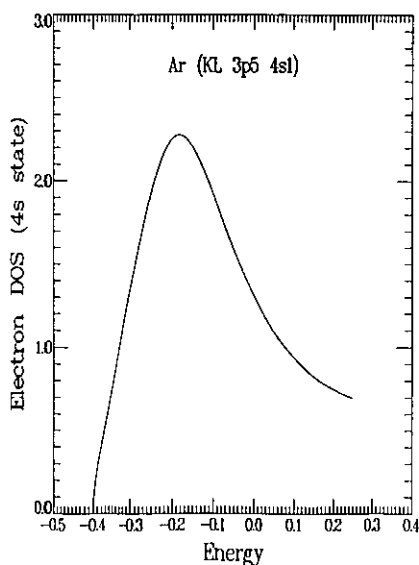


Figure 1. The electron DOS associated with the 4s state of the argon atom (KL 3s²3p⁵4s) embedded in a metal jellium characterized by the parameters (see [5, 6]) $V_{\text{bottom}} = -0.4$ au and $r_s = 5.0$ au.

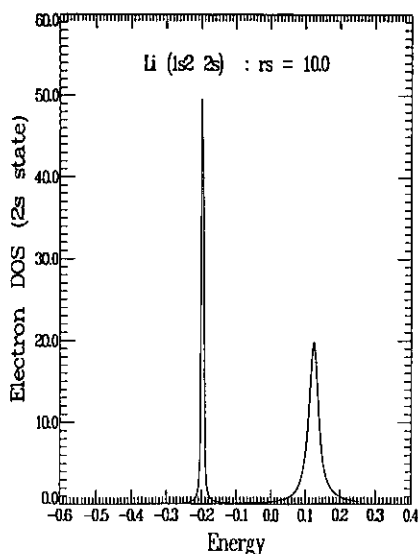


Figure 2. The electron DOS associated with the 2s state of a lithium atom ($1s^2 2s$) embedded in a metal jellium characterized by the parameters (see [5, 6]) $V_{\text{bottom}} = -0.4$ au and $r_s = 10.0$ au. The resonance that is exhibited at about 0.12 au is referred to as a 'ghost state' (see text).

In figure 2 we present a similar graph for the electron DOS associated with the 2s orbital of the Li ($1s^2 2s$) atom embedded in jellium of $V_{\text{bottom}} = -0.4$ au and $r_s = 10.0$ au. In this case, the peak of the electron DOS at -0.1975 au coincides with the real part of the eigenvalue of the 2s state as indicated in table 1. However, we observe an additional peak at about 8.8 eV higher which we cannot assign to any excited ($1s^2 n s$) state. The appearance of this unphysical state cannot be justified and we believe that it is more likely to reflect an artifact of the Green's function approach than a limitation of the Gaussian basis set used in our expansions.

In conclusion, we can argue that, in addition to the drawback that the Green's function approach reveals unphysical states whereas the direct-diagonalization method does not, our results indicate that the anticipated equivalence between the two described calculational approaches is only approximately valid for reasonably narrow resonances in agreement with the discussion that led to equation (2). On the other hand, the indicated equivalence [9] between the sub-space Hamiltonian technique [2] and the embedding scheme of Inglesfield [3] support our questioning the equivalence of the methodologies used to locate the resonances of a complex Hamiltonian. It appears that, when a complex-Hamiltonian approach is employed, a calculational scheme which directly solves equation (1) in the entire complex energy plane is unavoidable in the case of broad resonances of atoms and clusters embedded in metals. Thus we see the recent application [10, 11] of the CCM method in the determination of the resonances of chemisorbed atoms onto metal surfaces. Furthermore, the success of the CCM in predicting the atomic resonances gives support to our proposed calculational scheme [5, 6] which also solves directly and finds the eigenvalues of equation (1). As our scheme employs Inglesfield's embedding scheme [3] and the CHF methodology [7], it allows one to use jointly highly sophisticated

calculational techniques (band-structure and non-local Hartree-Fock or CI ones) which have been independently used in solid-state and atomic physics so far.

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