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INTRODUCING BOUND STATE RESONANCES INTO APPROXIMATE ATOM–SURFACE DIFFRACTION CALCULATIONS

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We present a method, based on projection techniques, for introducing bound state resonances into approximate methods, such as the quantum-sudden or semiclassical wave packet approaches, for the diffraction of atoms by periodic surfaces.

Exact calculations of the elastic diffraction of atoms by crystal surfaces are often lengthy numerical procedures, particularly when the incident energy is high, the surface corrugation is strong, or the unit cell is large [1–4]. On the other hand, simpler approximate treatments, although usually easier and numerically much shorter, often cannot handle properly the resonances with bound states. Here we suggest a method, based on projection operations, for introducing resonances into such a calculation. The need for simplified calculational procedures is quite evident since usually the interaction potential is inferred from a trial-and-error comparison of calculated and experimental intensities. This means that a short and inexpensive calculation, such as a semiclassical or sudden approach, is necessary as many calculational runs are usually required. However, bound state resonances can be very important features in the experimental data and are essential in determining the form of the potential in the region of the attractive adsorption well.

The bound state projection technique here proposed is a general approach and can be applied to various processes such as selective adsorption resonances in surface scattering and rotational and vibrational Feshbach resonances in gas phase scattering. In the following, the formulation of the method is given for atom–surface scattering. The application to gas phase processes is straightforward and will be discussed at the end of this note.

The projection method is most simply developed from the transition operator approach [5,6], although it can also be applied directly to the wave function. If the total interaction potential V is separated into the surface average contribution U plus a remainder v ,

$$V = U + v, \quad (1)$$

the reduced transition operator obeys the equation

$$t = v + vGt. \quad (2)$$

If we divide the projection operator P into two parts $P = P_1 + P_2$, eq. (2) appears as

$$t = v + vP_1Gt + vP_2Gt \quad (3)$$

and can be replaced by the equivalent pair

$$t = h + hP_2Gt, \quad (4)$$

$$h = v + vP_1Gh. \quad (5)$$

Now we assume that the projection operator P_2 projects out a small, finite subset of resonant discrete states of the surface averaged potential U ,

$$P_2 = \sum_d |\chi_d\rangle\langle\chi_d|. \quad (6)$$

The $|\chi_d\rangle$ are eigenstates of the surface averaged potential U . Then in matrix element form the pair of equations (4) and (5) become

$$h_{fi} = v_{fi} + \sum_l' v_{fl}(E_i - E_l + i\epsilon)^{-1} h_{li}, \quad (7)$$

$$t_{fi} = h_{fi} + \sum_d h_{fd}(E_i - E_d)^{-1} t_{di}, \quad (8)$$

where the sum in eq. (7) runs over the complete set of states of U except for the discrete states which appear in the sum of eq. (8). In eq. (8) a resonance is signaled by the denominator $E_i - E_d$ approaching zero, but this now poses no numerical problems because the t_{di} vanish simultaneously. For example, if only a single resonant bound state is projected we obtain

$$t_{fi} = h_{fi} + \frac{h_{fb}h_{bi}}{E_i - E_b - h_{bb}} \quad (9)$$

for the transition matrix from the initial state i to the final state f . For atom-surface scattering the intensity of the final scattered beam will be given by

$$I_f = \left| 1 - \frac{2i\pi m}{\hbar^2 \sqrt{k_{iz}k_{fz}}} t_{fi} \right|^2, \quad (10)$$

where t_{fi} is evaluated on the energy shell and k_{iz} and k_{fz} are the initial and final perpendicular wave vectors.

At this point, we recognize that there exists a restricted wave function equivalent to the restricted transition matrix of eq. (7). This restricted wave function, which we denote by $\Lambda_l^{(+)}(\mathbf{r})$ is the solution to the Schrödinger equation with the non-local projected potential $U + P_1 v$. The notation (+) on $\Lambda_l^{(+)}(\mathbf{r})$ signifies outgoing wave boundary conditions. Its major difference from the complete wave function corresponding to the t -operator of eq. (4) or (8) is that it contains no bound state resonances since intermediate coupling to the bound states has been projected out. Matrix elements of h such as those appearing in eq. (9) can be calculated according to

$$h_{nm} = (\chi_n | h | \chi_m) = (\chi_n | v | \Lambda_m^{(+)}), \quad (11)$$

where the χ_n are distorted states of U , including the bound states.

$$\chi_n = N_n e^{i(\mathbf{K}_i + \mathbf{K}_n) \cdot \mathbf{R}} \chi_{k_{nz}}(z), \quad (12)$$

where the $\chi_{k_{nz}}(z)$ are eigenstates of the one-dimensional potential U with z the direction perpendicular to the surface and \mathbf{R} parallel; N_n is the normalization coefficient.

The central point concerning the usefulness of the proposal presented in this paper is the assumption that there are approximate methods for obtaining the scattering wave function which produce an approximation to $\Lambda_l^{(+)}$ rather than to the true wave function. Various approximate methods may fit this description including the sudden approximation [7,8] and the recently developed time-dependent wave pocket method for surface scattering [9,10]. Both methods have been found to give accurate results at higher energies but their range of validity towards lower energies and the resonant regime is limited. In a recent study [11] the wave pocket approach has been found to "ignore" isolated resonances. In the sudden approximation, resonances are excluded altogether as it is based on uncoupled solutions of elastic wave functions. Nevertheless, in the regime of isolated resonances, these approximations may still provide a reasonable description of the overall intensity distribution and thus they can serve as a starting point for the present scheme.

The present proposal of projection methods may also be of use in exact coupled channel calculations. At lower scattering energies, asymptotically closed channels (diffraction or not-vib. states) have to be included in the calculation to obtain converged results. Selective adsorption or Feshbach resonances are always caused by coupling to these closed channels. On the other hand, these closed channels lead to numerical stability problems due to their exponentially growing behavior and frequent stabilization is often required to ensure linear independence of the solution. By projecting out the closed states, the numerical procedure is greatly facilitated. Later, those closed

states which couple to bound states and those leading to resonances can be projected back in.

Assuming that we have a reasonable approximation to the restricted wave function $\Lambda_i^{(+)}$ we can add the resonance back in and find a good approximation to the full transition matrix using eq. (8). Clearly, from eq. (8) or the simpler eq. (9), what is needed is to evaluate three classes of matrix elements h_{fi} , h_{fd} or h_{di} , and $h_{dd'}$ and then t_{fi} can be found by inversion of a small matrix whose size is equal to the number of discrete states which have been projected out.

We proceed to a discussion of how the various h -matrix elements can be evaluated from the wave function $\Lambda_i(\mathbf{r})$. The h_{fi} are the simplest as they are the coefficients of the asymptotic wave function from which one calculates the diffraction intensities of the projected potential $U + P_1 v$

$$\Lambda_i^{(+)}(\mathbf{R}, z \rightarrow \infty) = e^{i\mathbf{K} \cdot \mathbf{R}} (e^{-ik_{iz}z} - e^{ik_{iz}z}) + \frac{2\pi i m}{\hbar^2} \sum_{\mathbf{K}} \frac{h_{fi}}{k_{fz}} e^{i(\mathbf{K}_i + \mathbf{K}) \cdot \mathbf{R}} e^{ik_{fz}z}, \quad (13)$$

where capital letters denote vectors parallel to the surface and $k_{fz}^2 = K_i^2 + k_{iz}^2 - (\mathbf{K}_i + \mathbf{K})^2$.

The h_{di} are also straightforward and are perhaps most readily evaluated from direct integration of the matrix element

$$h_{di} = (\chi_d^{(-)} | v | \Lambda_i^{(+)}), \quad (14)$$

where the distorted state χ_d is readily calculable.

The matrix elements h_{fd} pose slightly more of a problem because the states Λ_d are not generally calculated by the semiclassical method. (If these states were calculable the method would be essentially exact and there would be no need for the propositions described herein.) However, we can make use of the fact that on the energy shell we have

$$h_{fd} = (\chi_f^{(-)} | v | \Lambda_d^{(+)}) = (\Lambda_f^{(-)} | v | \chi_d^{(+)}) \quad (15)$$

and the calculation is the same as (12) above except that it requires the additional calculation of $\Lambda_f^{(-)}$, which is the incoming wave function of the projected potential $U + P_1 v$. Since in most cases the resonances appear very close to the energy shell it is reasonable to approximate h_{fd} in this small region near the energy shell by the far right hand side of (15).

The final matrix elements to evaluate are the $h_{dd'}$, which as illustrated in eq. (9) give the energy shift and lifetime of the resonance

$$h_{dd'} = (\chi_d^{(-)} | v | \Lambda_{d'}^{(+)}). \quad (16)$$

If the states Λ_d are unavailable, this cannot be calculated directly, but it can be evaluated indirectly through the defining equation (7)

$$h_{dd'} = v_{dd'} + \sum_l' v_{dl} (E_i - E_l + i\epsilon)^{-1} h_{ld'}. \quad (17)$$

Since all resonant discrete states are already projected out of the sum in eq. (15) we can ignore the remaining discrete states and sum over continuous states only. Then $h_{ld'}$ can be evaluated from (13) above. Further approximations that simplify the evaluation of (15) are to keep only the δ -function or energy conserving contribution to the integral; or to let $h_{ld'} \approx v_{ld'}$, the first-order development. Both of these approximations have been shown to be very useful and to produce reliable results in many cases [12,13]. The signature of an isolated resonance is an intensity lineshape containing two extremes, a maximum and a minimum. It can be readily shown that this is the case starting from the form of the t -matrix and intensity in eqs. (9) and (10) [12,14].

This completes the exposition of the method. To review, we assert that approximate methods which do not take account of bound states may be considered as solutions corresponding to the restricted transition matrix h_{fi} of eq. (7), these matrix elements being obtained from the coefficients of the asymptotic wave function as in eq. (11). The diffraction intensities with bound state resonance effects are calculated from (10) with the true transition matrix t_{fi} given by resolving the finite and usually small system of linear equations (8). The various h -matrix elements appearing in eq. (8) can be evaluated to a good approximation as shown in eqs. (11) through (15).

The application of this proposed technique is not restricted to atom-surface scattering. Bound state resonances play an important role in inelastic atom-molecule scattering processes as well [15]. There the resonances occur through coupling between rotation or vibrational states of the target molecule and bound states of the atom-molecule compound. Use of the projection method for these processes is straightforward. The bound states of the orientational averaged atom-molecule compound potential can be projected out. Again a sudden or semiclassical or reduced coupled channels calculation could be used to obtain the restricted wave function $\Lambda_i^{(+)}$. The role of the diffraction states for surface scattering would be played by the rotational or vibrational target states. The scattered plane wave [see eq. (11)] would be replaced by a radial function representing a spherical wave with the proper wave vector k_α where α denotes a molecular quantum member. Then for each partial wave, the outlined procedure could be used. The theoretical methods outlined in this note provide for the possibility of using very quick and efficient ways of calculating elastic diffraction intensities while still allowing for the possibility of calculating all bound state resonances.

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