

Theoretical Correlation of Intensity Features of Selective Adsorption with Fourier Components of the Atom-Surface Potential

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Rules governing intensity features of selective adsorption data are derived. Minima or mixed maxima-minima in the specular intensity are predicted for resonant channels that strongly couple to the specular, and maxima for resonance states that couple only indirectly to the specular. These rules, which facilitate the identification of resonance positions and intensity features, are corroborated by available experimental data. Resonance shifts are also calculated. The characteristic asymmetric splitting of overlapping resonances is accounted for.

The purpose of this Letter is to present an approximate derivation of general rules which correlate features of the intensity of atom-surface scattering near selective adsorptions with Fourier components of the interaction potential. These rules for isolated resonance may be summarized as follows: (1) Specular minima will be observed when the channel in resonance couples directly and strongly to the specular channel (more strongly than through indirect coupling), and to at least one other open channel. (2) Mixed extrema (maxima being predominant) in the specular intensity will be observed when the only open channel to which the resonant state couples strongly and directly is the specular. (3) Specular maxima will be observed for resonant channels that couple only indirectly to the specular through the strong Fourier components.

These rules suggest that the important features of the intensity are determined by the coupling rather than by other dynamical properties (incoming angle, energy, etc.). The rules are useful in identifying the important components of the atom-surface potential, for qualitative data interpretation, and for making predictions about new systems. The derivation assumes purely elastic scattering; strong inelastic effects would affect our results. No explicit form for the atom-surface interaction is necessary. We use an expansion method related to Feshbach's^{1,2} theory of nuclear resonances. The rules, however, appear to have greater generality than this approximate

derivation would indicate. Numerical calculations relying on specific model potentials (i.e., the attractive hard wall) also agree with our predictions. The relationships derived here between potential form and intensity behavior have not been demonstrated in these calculations because of their numerical nature. Results explaining the asymmetric splittings of overlapping resonances are also discussed.

The atom-surface potential is periodic and can be expanded as

$$V(\vec{X}, z) = V_0(z) + \sum_{\vec{G} \neq 0} V_{\vec{G}}(z) e^{i\vec{G} \cdot \vec{X}}, \quad (1)$$

where $\vec{X} = (x, y)$ denotes a position vector in the plane of the surface, z is the direction normal to the surface, and \vec{G} are surface reciprocal lattice vectors. The scattering channels are denoted by wave vector $\vec{k}_{\vec{G}} = (\vec{K}_{\vec{G}}, k_{\vec{G}})$. We adopt the notation $\vec{k} = (\vec{K}, k_{\vec{G}}) \equiv (\vec{K}_0, k_{0\vec{G}})$ for the specular channel and $\vec{k}_i = (\vec{K}, -k_{\vec{G}})$ for the incident channel. $\vec{K}_{\vec{G}} = \vec{K} + \vec{G}$ gives the diffraction condition.

We write the Hamiltonian for the system as $\mathcal{H} = \mathcal{H}_d + V_p$, where

$$\mathcal{H}_d = (-\hbar^2/2m)\nabla^2 + V_0(z), \quad (2)$$

$$V_p = \sum_{\vec{G} \neq 0} V_{\vec{G}}(z) e^{i\vec{G} \cdot \vec{X}}.$$

The eigenfunctions for the Hamiltonian \mathcal{H}_d are denoted by $\langle \vec{X}, z | \vec{K}_{\vec{G}}, k_{\vec{G}} \rangle$ for the continuum states and $\langle \vec{X}, z | \vec{K}_{\vec{G}}, n \rangle$ for the bound states.

The spectral representation of the Green's function G_d^+ in terms of the eigenvectors of \mathcal{H}_d is given by

$$G_d^+ = \lim_{\epsilon \rightarrow 0} \sum_{\vec{G}} \int dk_{\vec{G}}' \frac{|\vec{K}_{\vec{G}}, k_{\vec{G}}'\rangle \langle \vec{K}_{\vec{G}}, k_{\vec{G}}'|}{E - E_{\vec{K}_{\vec{G}}, k_{\vec{G}}'} + i\epsilon} + \sum_{\vec{G}, n} \frac{|\vec{K}_{\vec{G}}, n\rangle \langle \vec{K}_{\vec{G}}, n|}{E - E_{\vec{K}_{\vec{G}}, n}}. \quad (3)$$

In the distorted-wave Born (DWB) method³ the integral equation for the eigenvector $|\Psi_{\vec{K}}\rangle$ of the total Hamiltonian \mathcal{H} is iterated. It is apparent from Eq. (3) that (near a selective absorption) when $E - E_{\vec{K}_{\vec{G}}, n} = 0$ the DWB series leads to infinite transition amplitudes. In order to move these singularities off the

real energy axis we introduce the projector

$$Q = \sum_{\vec{k}_Q, n_Q} |\vec{k}_Q, n_Q\rangle \langle \vec{k}_Q, n_Q|$$

which projects onto the states which are in resonance. $P = I - Q$ contains all the continuum states. Solving the two coupled equations for $P|\Psi_k^+\rangle$ and $Q|\Psi_k^+\rangle$, then looking at the long-range behavior of $P|\Psi_k^+\rangle$, we find that the transition probabilities are given by

$$P_{\vec{k}_Q \leftarrow \vec{k}_i} = (k_{Qz}/k_z) |\delta_{\vec{k}_Q, \vec{k}} + \sigma_{\vec{k}_Q \leftarrow \vec{k}_i}^d + \sigma_{\vec{k}_Q \leftarrow \vec{k}_i}^r|^2 \quad (4)$$

with direct and resonant scattering terms

$$\sigma_{\vec{k}_Q \leftarrow \vec{k}_i}^d = \langle \vec{k}_Q, k_{Qz} | PV_p P | \Lambda_{\vec{k}}^+ \rangle 2\pi m / i \hbar^2 k_{Qz}, \quad (5)$$

$$\sigma_{\vec{k}_Q \leftarrow \vec{k}_i}^r = \langle \Lambda_{\vec{k}}^+ | PV_p Q [Q(E - \mathcal{H} - W)Q]^{-1} QV_p P | \Lambda_{\vec{k}}^+ \rangle 2\pi m / i \hbar^2 k_{Qz},$$

where $W \equiv V_p P (1 - PG_d^+ V_p P)^{-1} PG_d^+ V_p$. Equations (5) are exact expressions. $|\Lambda_{\vec{k}}^+\rangle$, however, is the eigenvector for the Hamiltonian $P\mathcal{H}P$ and is difficult to evaluate. In the following we calculate it via an expansion in $PV_p P$.

We now discuss how the features of the specular intensity in the vicinity of an isolated resonance can be correlated with the Fourier components of the interaction potential. For an isolated resonance, Q may be chosen to contain only one resonance state, $Q = |\vec{k}_Q, n_Q\rangle \langle \vec{k}_Q, n_Q|$. We consider three cases.

Case 1.—If we assume that $V_p(\vec{X}, z)$ couples $|\vec{k}_Q, n_Q\rangle$ directly to the specular state and expand to lowest order, $\sigma_d \equiv \sigma_{\vec{k}_Q \leftarrow \vec{k}_i}^d$ and $\sigma_r \equiv \sigma_{\vec{k}_Q \leftarrow \vec{k}_i}^r$ for the specular intensity are given by

$$\sigma_d = \langle \vec{k}, k_z | V_p PG_d^+ V_p | \vec{k}, k_z \rangle 2\pi m / i \hbar^2 k_z, \quad \sigma_r = \frac{\langle \vec{k}, k_z | V_p |\vec{k}_Q, n_Q\rangle \langle \vec{k}_Q, n_Q | V_p | \vec{k}, k_z \rangle}{E - E_{\vec{k}_Q, n_Q} - \delta + i\Gamma/2} \frac{2\pi m}{i \hbar^2 k_z}, \quad (6)$$

where $\delta = \text{Re} \langle \vec{k}_Q, n_Q | V_p PG_d^+ V_p | \vec{k}_Q, n_Q \rangle$ gives the shift and Γ describes the resonance width:

$$\Gamma = \sum_{\substack{\vec{k}_Q \\ \text{open} \\ \text{channels}}} \langle \vec{k}_Q, n_Q | V_p | \vec{k}_Q, k_{Qz} \rangle \langle \vec{k}_Q, k_{Qz} | V_p | \vec{k}_Q, n_Q \rangle 2\pi m / \hbar^2 k_{Qz}. \quad (7)$$

In a region where the scattering is predominantly specular σ_d will be small and can be neglected. With the assumption that at least one open channel besides the specular couples directly to the state in resonance, Eq. (4) predicts a minimum in the specular intensity at $E - E_{\vec{k}_Q, n_Q} - \delta = 0$ with width Γ . Unlike earlier perturbation theories⁴ this elastic theory predicts the experimentally observed specular minima. When σ_d is included (as long as the scattering is mostly specular) a minimum is still predicted but now a small shoulder appears on one side of the minimum.

Case 2.—For the case where no open channel other than the specular couples directly to $|\vec{k}_Q, n_Q\rangle$, σ_d and σ_r are as given above except that the sum Γ , Eq. (7), contains only one term. Equation (4) now gives a mixed-extrema structure in the specular intensity. This is because the shape of the intensity in the vicinity of the resonance is due entirely to the term $\sigma_d \sigma_r^* + \sigma_d^* \sigma_r$, which has a minimum on one side of $E - E_{\vec{k}_Q, n_Q} - \delta = 0$ and a maximum on the other. The predominant feature is the maximum which is closer to $E - E_{\vec{k}_Q, n_Q} - \delta = 0$.

Case 3.—Consider a resonant state that couples only indirectly to the specular; for example, a $(\frac{1}{n})$ -type resonance where only $V_{01}(z)$ is large in the interaction potential. [We shall use the notation $(\frac{i}{n})$ for bound-state resonances where (i, j) specifies the diffraction channel and n the bound-state energy level.] To calculate the intensity behavior, higher-order terms must be included. σ_d and σ_r are as given in Eq. (6) except that the terms in the numerator of σ_r become $\langle \vec{k}, k_z | V_p | PG_d^+ V_p | \vec{k}_Q, n_Q \rangle \equiv \xi$. If $|\text{Im} \xi| \gg |\text{Re} \xi|$, Eq. (4) predicts a maximum as the predominant resonant feature. This assumption is found to be valid for the Morse potential. When v_{11} is included for a $(\frac{1}{n})$ resonance we have shown that the maximum behavior persists until v_{11} is of the order of v_{01} . When $v_{11} = v_{01}$ we predict a minimum which agrees with the results of Finzel *et al.*⁵

We have checked the generality of these low-order results by comparison with experimental data, the convergent results of Harvie and Wear, and the numerical results of Chow and Thompson.⁷ In every case the rules are corroborated by the

measured or calculated results even in the regions where the expansion would not be expected to be reliable.⁸ Very recently Frankl and co-workers⁹ have done a detailed experimental study of these predictions for He-LiF scattering. An example of their data demonstrating the rules derived here is given in Fig. 1. Note the appearance of minima for (0_n^1) resonances and maxima for (0_n^2) and (1_n^1) resonances. Calculations^{10,11} have predicted that $V_{02}(z)$ and higher components of the atom surface potential are small relative to $V_{01}(z)$ in He-LiF, and therefore our rules predict (0_n^1) minima and (0_n^2) maxima, both of which are exhibited. The (1_n^1) resonances also appear to be maxima. This would indicate that $V_{11}(z)$ for LiF is also small compared to $V_{01}(z)$ which is contrary to surface potential calculations which predict $v_{11} \approx v_{01}$. This result, however, is consistent with other data of Frankl¹² which show no splitting of the (0_1^1) and (1_1^1) resonance near the 45° azimuth of LiF. It is also consistent with the detailed analysis of Harvie and Weare⁶ and Garcia.¹³ An interesting further example is given in the close-coupling results of Chow and Thompson⁷ where a large v_{11} was included. The calculation was done for $\theta = 65^\circ$ but it may be qualitatively compared to the data of Frankl included here in Fig. 1. In the $\varphi = 45^\circ$ region we see that when a large v_{11} is included, minima in the specular intensity are calculated, whereas experimentally maxima are measured. Data supporting rule 2 have been reported by Frankl *et al.*⁹ Maxima for (1_0^1)

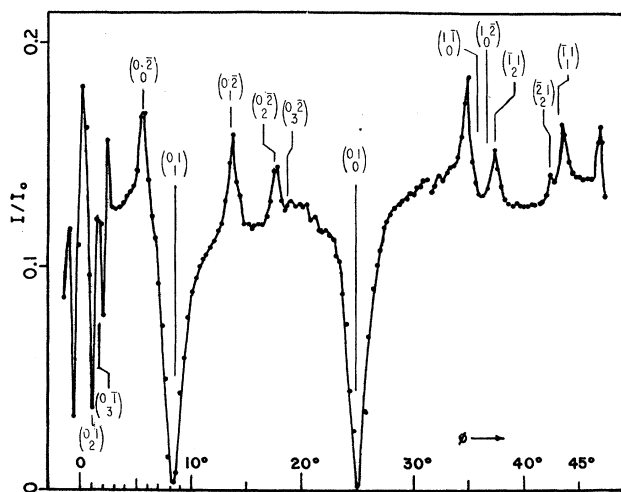


FIG. 1. Data of Frankl *et al.* (Ref. 9). Specular intensity versus azimuthal angle for He ($\lambda = 1.09 \text{ \AA}$) on LiF(100) at $\theta = 70^\circ$. Vertical marks are calculated positions of selective adsorptions as assigned by Frankl.

resonance were observed at $|k| = 5.76 \text{ \AA}^{-1}$ and $\varphi = 0^\circ$ for He-LiF where the $(1, \pm 1)$ channels are closed and the only open channel that couples directly to $(1, 0)$ is the specular. Other data supporting these rules are those of Boato, Cantini, and Tatarek¹⁴ for He-graphite and of Finzel *et al.*⁵ for LiF and NaF.

Because of the approximate nature of this derivation there is no assurance that these rules will apply to all selective-adsorption data. The apparent agreement with existing data and numerical results suggests that there may be a more general derivation that would include a wider class of experiments.

In addition to the qualitative features above, the theory also provides a method for calculating resonance shifts and the splitting of overlapping resonances. Recent calculations have neglected these terms. As noted in Harvie and Weare⁶ these shifts must be included in order to accurately fit the data and evaluate bound-state energies. We have computed the shift for the He-LiF (0_0^1) resonance for data of Meyers and Frankl¹⁵ at $\theta = 70^\circ$. For computational convenience we assumed the Morse potential, $V_0(z) = D \exp(-2az) - 2D \exp(-az)$, and a perturbation potential, with $V_G(z) = v_G D \exp(-2az)$ where only v_{01} and v_{11} are nonzero. For comparison with the results of Harvie and Weare we used the parameters $D = 8.22 \text{ meV}$ and $a = 1.1 \text{ \AA}^{-1}$ which give four bound-state energy levels: $\epsilon_n = -6.1, -2.8, -0.8, \text{ and } -0.01 \text{ meV}$. Using $v_{01} = 0.1$ and $v_{11} = 0$ we calculate that the (0_0^1) resonance position is shifted by 0.6° which is in excellent agreement with the actual position of the resonance, and is in agreement with the results of Harvie and Weare. For these scattering angles and energies, we find that essentially all the shift is from the coupling of other bound states to (0_0^1) . Higher-order corrections to the shift have been estimated to be of the order of 15% by methods of Ref. 3.

As noted by Chow and Thompson,¹⁰ when bound-state resonances cross, the degeneracy may be removed by band splitting. To analyze these data, we select Q to contain all states which are in resonance. For the crossing of two states $|n\rangle$ and $|m\rangle$ the poles of σ_r are found at the zeros of the determinant

$$\begin{vmatrix} E - E_n - \delta_n + i\Gamma_n/2 & -V_{n,m} \\ -V_{n,m} & E - E_m - \delta_m + i\Gamma_m/2 \end{vmatrix}. \quad (8)$$

Since $V_{nm} = \langle n | V_p + V_p P G_d^+ V_p + \dots | m \rangle$ there is band splitting even in situations where there is no Fourier component directly coupling the states.

We note that the positions of the zeros in Eq. (8) are affected by the shifts δ_n and δ_m . The splitting from Eq. (8) can be used to calculate accurately the magnitude of the Fourier components of the potential. Since the magnitude of the splitting does not seem to be dependent on surface temperatures, the evaluation of the Fourier com-

ponents of the potential from selective adsorption may be more accurate than evaluation from temperature-dependent diffraction intensities. Using the data¹⁶ for NaF in the symmetry direction $\varphi = 45^\circ$, the shift of a $\binom{01}{0}\binom{10}{0}$ resonance can be used to estimate the potential parameter v_{11} . Because the (i, j) and (j, i) channels are degenerate, σ_r in lowest order for this case becomes

$$\sigma_r = \frac{2\langle \vec{K}, k_z | V_p | 0 \rangle \langle 0 | V_p | \vec{K}, k_z \rangle}{E - E_{01,0} - \delta + i\Gamma/2 - \langle 0 | V_p + V_p P G_d + V_p | 0 \rangle} \cdot \frac{2\pi m}{i\hbar^2 k_z}, \quad (9)$$

giving rise to one specular minimum with shift at 45° , from Eq. (8),

$$\delta_{45^\circ} = \langle 0 | V_p | 0 \rangle + \text{Re}(\langle 0 | V_p P G_d + V_p | 0 \rangle + \langle 0 | V_p P G_d + V_p | 0 \rangle). \quad (10)$$

The first term in Eq. (10) is a direct-coupling term. Using $v_{01} = 0.1$, we find that $v_{11} = 0.03$ shifts the resonance to the experimentally observed position. In this case the three terms in Eq. (10) contribute 0.5° , 0.25° , and 0.1° , respectively, to the total shift of 0.85° .

The importance of the shifts which are due to coupling with the continuum and other bound states not in resonance to data interpretation is evident in terms of the asymmetric displacements of the minima about the calculated resonance position. An example of this behavior is given in Hoinkes, Greiner, and Wilsch.¹⁷

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