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Multiadatom effects in the chemisorption energy of ordered overlayers*

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The indirect interaction energy per adatom is evaluated for a $c(2\times 2)$ overlayer in a model system, and is found to be very well approximated by (twice) the next-nearest-neighbor pair interaction energy, verifying the validity of earlier work. Three adatom (nonpairwise) interaction energies are also considered; while insignificant for total interaction energies, they are comparable to more-distant (viz., third-) neighbor pair interactions.

An explanation of ordered overlayers of adatoms on transition metals was given by Einstein and Schrieffer[1] (ES) in terms of an indirect interaction between individual pairs of adatoms. In this picture all adatoms bind in one particular coordination site (atop, centered, or bridge) for any coverage less than saturation (since the difference in energy between these sites will be greater than inter-adatom energies). The pair interaction energy (that is, the energy difference between two adatoms at (nearby) sites and twice the energy of a single adatom on the surface)[2] is anisotropic, oscillatory, and very rapidly decaying with separation; thus, the adlayer superlattice structure is determined by the nearest attractive pair interaction. Multi-adatom interactions were seemingly a smaller-order effect. In marked contrast, subsequent studies[3,4] (within the same model) of changes of density of states for a complete ordered overlayer showed that even qualitative features could arise which could not be decomposed into pair effects. The pair effects were often comparable to one-adatom effects rather than smaller by over an order of magnitude (as is the case for energies). Moreover, trio (three-adatom nonpairwise) effects could be comparable in magnitude to pair effects. In short, the situation for changes in density of states is poorly convergent. Hence we undertook calculations of trio and ordered overlayer energetics to verify that the previously reported viewpoint was justified in describing adlayer patterns.

In the sample model of ES the substrate is described by a single-band tight-binding model, with the diagonal site energy giving the energy zero and the nearest-neighbor hopping $-\frac{1}{2}$ establishing the enrgy unit as one-sixth the bandwidth (and so 1 or 2 eV for transition metals). For simplicity and specificity we here consider the adatom in the atop position; the generalization to bridge or centered binding is available in ES and elsewhere. The adatom couples to the orbital on its nearest substrate neighbor with hopping matrix element $-V$.

The present model characterizes the adatom by a single nondegenerate energy level E_a; Coulomb effects might be included in the restricted Hartree-Fock sense, namely, $E_a = E_a^0 + U\langle n_{a\sigma}\rangle$, where E_a^0 is the energy of the vacant orbital, U is the Anderson[5] intra-adatomic Coulomb repulsion, and $\langle n_{a\sigma}\rangle$ is the average occupancy of the adatom for one spin direction. ES estimated E_a as roughly the average of the ionization and the affinity levels (i.e., $\langle n_{a\sigma}\rangle = \frac{1}{2}$, neutral adsorption), as in many chemical molecular-orbital calculations.[6] Pandey[7] has used a more elaborate "chemical-transferability" scheme: he adjusts the adatom and adatom-substrate parameters so that cluster computations of small molecules involving the relevant elements fit levels found in photoemission experiments; presumably similar parameters hold in chemisorption systems. If one views all self-consistency problems as focused on the adatom, one can stay with the Anderson model[5] and solve self-consistently for $\langle n_{a\sigma}\rangle$. Typically this has been pursued in Hartree-Fock, either in the restricted form[8] ($\langle n_{a\uparrow}\rangle \equiv \langle n_{a\downarrow}\rangle$ as an ansatz) suggested above or in an unrestricted version.[9,10] However, when the latter suggests a local moment on the adatom, Hartree-Fock is known to fail.[11] More recently, Brenig and Schönhammer[12] and other researchers[13] have given more detailed treatments of the Anderson model as applied to single-atom chemisorption.

The other approach to self-consistency is less satisfactory. Since the linear-combination-of-atomic-orbitals (LCAO) ansatz fixes electron orbitals, self-consistency is phrased in terms of Friedel's sum rule[14]—which here requires total charge neutrality with some finite range of the adatom—rather than Poisson's equation.[15] Some diagonal (in occupation-number space) perturbation is added typically to the adatom energy E_a (Refs. 16–18) (which means essentially that E_a becomes a derived rather than free parameter) and often to its nearest neighbor(s) on the surface.[16,17] Sometimes off-diagonal Coulomb terms are also included in various ways.[17,18] Generally,[18] neutrality is required either at each site[16,17] (essentially the old

"minimum-polarity" principle of ferromagnetic theory[19]) or just in the surface cluster consisting of the adatom and its nearest neighbor(s).[16,20] These approaches exclude the possibility of any longer-range oscillations, and thus tend to overcorrect. The substrate perturbations can also produce new surface states.[21] The quantitative results are rarely compelling, and the qualitative ones could usually be written without the numerics.[22]

Fortunately Schönhammer, Hartung, and Brenig[23] have shown that in calculations of pair-interaction energies (in stark contrast to single-adatom binding energies), a very careful treatment of Coulomb effects leads to curves that are almost the same as the Hartree-Fock ones. This similarity is really not that unexpected; Grimley and Walker[24] pointed out that while considerable charge transfer might take place during chemisorption, little more should happen as a function of the relative orientation of chemisorbed atoms.

For three adatoms bound to sites 1, 2, and 3, the formula for their interaction (the difference between the energy of three adatoms in these relative positions and thrice the energy of one adatom) can be derived from the matrix expressions of ES or otherwise,[24] and is

$$\Delta W = -\frac{2}{\pi}\int_{-\infty}^{E_F} dE \tan^{-1}\left(1 - \frac{V^4(G_{12}^2+G_{23}^2+G_{13}^2)}{(E-E_a-V^2G_{11})^2} - \frac{2V^2G_{12}G_{23}G_{13}}{(E-E_a-V^2G_{11})^3}\right). \quad (1)$$

Here G_{ij} is the advanced Green's function between sites i and j on the surface of the semi-infinite substrate. The 1-2 pair interaction between adatoms on sites 1 and 2, may be obtained from this expression by setting G_{23} and G_{13} to zero. In this framework, the trio interaction is defined as Eq. (1) minus the 1-2, 1-3, and 2-3 pair interactions. This approach can obviously be continued, but it produces increasingly large noise from the computation of the individual G's. As observed by Grimley and Walker[24] there is no simple way to write down trio (or further multiple) adatom interactions.

From another vantage, we can easily write the interadatom interaction energy per adatom for a complete (1×1) ordered overlayer:

$$\Delta W = -\left(\frac{2}{\pi N_a}\right)\sum_{k_\parallel}\int_{-\infty}^{E_F}\tan^{-1}\left(1 - \frac{V^2(G(k_\parallel,E)-G_{11}(E))}{E-E_a-V^2G_{11}(E)}\right)dE\,, \quad (2)$$

where the summation goes over the surface Brillouin zone (SBZ), $G(k_\parallel,E)$ is the two-dimensional inverse Fourier transform of the G_{ij}, and N_a is the number of adatoms. In this case, the neglect of the direct interaction is particulary questionable. We therefore focus attention on the $c(2\times 2)$ overlayer. In this case, since the real space unit cell area is doubled, the summation over $k_\parallel$ extends over only a reduced SBZ with half the size; for a square-surface (reciprocal) lattice, the natural choice is an inscribed "diamond" (square rotated by 45°, with sides $1/\sqrt{2}$ times the original side). Clearly, this leads to a folding of the parts of the highly blurred [$E_{surf}(k_\parallel)$ covers a wide range] band structure outside the diamond back into the diamond (in analogy to the formation of optical phonon modes in a Bravais lattice by changing the mass on alternate ions), producing a structure of two fuzzy bands which overlap for some values of $k_\parallel$. For the change in density of states due to $c(2\times 2)$ chemisorption, one finds considerable complications (including localized states between as well as outside the bands),[3,25] which we will explore carefully elsewhere.[26] For present purposes, we note that for a $c(2\times 2)$ rather than (1×1) adlayer the only modification of Eq. (2) besides changing the limits of the $k_\parallel$ sum is to replace $G(\vec{k}_\parallel,E)$ by the average of it and its complementary point outside the diamond, namely (taking advantage of the symmetries of the problem), by

$$\tfrac{1}{2}\{G(\vec{k}_\parallel,E)+G(\pi(1,1)-\vec{k}_\parallel,E)\}.$$

So far all we have required of the substrate lattice is that it have a two-dimensionally infinite square-lattice face: it could be a semi-infinite crystal or a slab; its bulk point-group symmetry could be simple cubic, fcc, or bcc (or for that matter primitive or body-centered tetragonal). To make contact with previous work we take the (100) face of a simple cubic crystal. Obviously this choice will not allow quantitive statements about the fivefold degenerate d band of bcc or fcc transition metals, but this choice is no worse and in some ways better than single-band bcc or fcc crystals, since these contain sharp idiosyncratic structure in their densities of states (sometimes leading to spurious peaks in their chemisorption-induced changes in densities of states[27]) while the (100) simple cubic crystal has the simple broad struc-

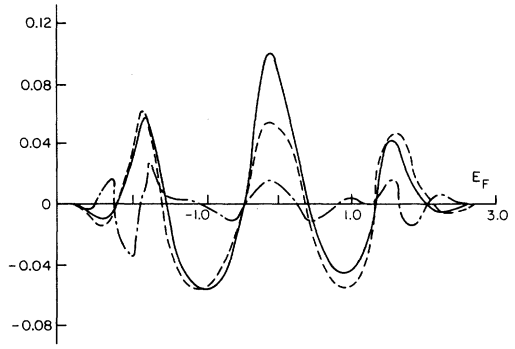

FIG. 1. Interaction energy vs Fermi energy for intermediate ($V = \frac{3}{2}$) adatom-substrate hopping and adatom energy near the center of the band ($E_a = -0.3$). The solid line gives the energy per adatom for a complete $c(2\times 2)$ overlayer. The dashed line is the sum (per adatom) of all pair contributions; it is dominated by the next-nearest-neighbor pair. The dash-dot curve is the weighted sum of the trio interaction (three-adatoms minus constituent pairs) for the two configurations containing two next-nearest-neighbor pair components (see text).

ture one would like the substrate to present in a model calculation.

Figure 1 displays the essence of the present computations. We plot interaction energy versus substrate band filling (Fermi energy). The curve labeled "pairs" is an explicit pair-by-pair sum of the closest pairs that arise in the $c(2\times 2)$ structure, since no analytic summation is possible. (That is, we could pick one adatom, find and sum the pairs, contain it and all other adatoms in a large domain, and then divide by two; obviously, this task can be eased by taking advantage of the fourfold symmetry of the pattern.) A closer examination[26,28] shows that this pair curve is dominated by the closest diagonal (next-nearest-neighbor) pair interaction, as indicated in ES. The next smaller pair interaction in the $c(2\times 2)$ adlayer [third-nearest neighbor of the square (100) face] is generally less than a quarter the magnitude of the dominant pair. The "pairs" curve closely parallels the corresponding curve for the complete $c(2\times 2)$ pattern, and would give a good quantitative representation of it except near the center of the band. Thus the nearest attractive pair explanation promulgated by ES is confirmed.

In the $c(2\times 2)$ pattern, there are two types of three-adatom arrangements involving two next-nearest-neighbor ($\langle 11\rangle$) pairs: collinear (so that the third pair is $\langle 22\rangle$) and right isosceles triangle (so that the third pair is $\langle 20\rangle$). Computations show that the two trio interactions from these arrangements have comparable magnitude which in turn is nearly an order of magnitude greater than trios containing one or no nearest diagonal neighbors. In Fig. 1, the trio curve gives the trio interaction per adatom for these two dominant arrangements, with appropriate weightings for the number of ways in which they arise in the $c(2\times 2)$ pattern. The curve is usually in the correct direction to correct discrepancies between the pair and $c(2\times 2)$ curves, but it is often too large in magnitude. This overcorrection might be expected from considerations similar to those leading to Friedel-like oscillations. For many values of E_F, then, one actually does worse in reproducing the $c(2\times 2)$ curve by adding three-adatom effects above to the pair curve.

The magnitude of dominant trio interactions is often comparable to the magnitude of the third-nearest pair interaction energy. For most phenomena (e.g., the order-disorder transition of the overlayer) and at room temperatures, these interactions are inconsequential, but at low temperatures these energies will be important in determining the shape of islands at presaturated coverages.[26,28] It would therefore be of considerable interest to obtain values for the energies of these trio and weaker pair interactions in more realistic representations of substrates.

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