SURFACE SCIENCE LETTERS

THE THREE-ADATOM NON-PAIRWISE ("TRIO") INTERACTION, WITH IMPLICATIONS FOR MONTE CARLO SIMULATIONS OF O/W(110)

Theodore L. EINSTEIN

University of Maryland, Department of Physics and Astronomy, College Park, Maryland 20742, USA

Ching et al. * found that three-adatom non-pairwise interactions, with a repulsive energy greater than a quarter the nearest pair attraction, can explain the pronounced asymmetries in the phase diagram of O/W(110). In the first explicit calculations of such short-range "trio" interactions, we find that electronic indirect interactions have strengths consistent with their parameters. In general the closest-spaced trios are stronger than all but the few shortest-range pair interactions which determine the adlayer symmetry. We further show that triad configurations with similar shorter legs should have comparable magnitude; when applied to O/W(110), this idea doubles the number of trios entering the equations of Ching et al. * and thus can halve the minimum required trio strength. Such trio interactions (as well as linear triad configurations) have a substantial quantitative effect on the pair interaction strengths extracted from Monte Carlo simulations.

The lattice gas model has become the accepted description of many chemisorption systems; it underpins the Monte Carlo computations used to simulate adatom order–disorder transitions [1–7]. The particular model for O/W(110) considered by Ching, Huber, Lagally, and Wang [6] (hereafter CHLW) is described in the upper portion of fig. 1. Near half a monolayer, the adatoms form a (2 X 1) superlattice at lower T; one domain is illustrated. This structure is produced by the strongly attractive pair interaction E_1 and the strongly repulsive E_2 indicated [8]. The more-distant pair interactions are needed to produce the observed compact patches, rather than isolated rows, at low coverages. With only pair interactions, a lattice gas model produces a phase diagram symmetric about half a monolayer [2] in analogy to the up–down symmetry of the Ising model. Such is rarely if ever true in experiment [9–11]. Three-adatom interactions lift this symmetry. CHLW chose [just] the two triads indicated by solid lines. To account for the presence of (2 X 2) ordering at $\theta = 3/4$ but not $\theta = 1/4$, (the average of) these trio (three-adatom, non-pairwise) interaction energies then must be repulsive, with strength at least $|E_1|/4$ [6].

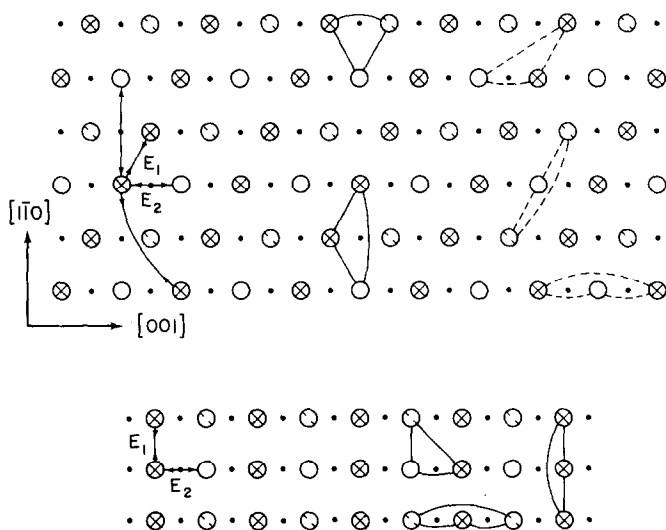* W.Y. Ching, D.L. Huber, M.G. Lagally and G.-C. Wang, Surface Sci. 77 (1978) 550.

Fig. 1. The top panel is a schematic of the lattice gas model for O on W(110), after ref. [6]. The large circles indicate the supposed adsorption site, consistent with LEED [8]; a bridge position between two W's, indicated by dots, 3.16 Å apart. The X's indicate occupied sites in one domain of the p(2 × 1) adlayer. The dashed slashes indicate sites that could be subsequently filled to form the p(2 × 2). On the left are sketched the pair interactions between sites used in ref. [6] to describe the disordering of the p(2 × 1) overlayer. The solid triangles in the center are the trios used in ref. [6] to understand the p(2 × 2) high coverage phase. (N.B. the top panel is slightly distorted, with the ratio of vertical to horizontal scale 27% too large.) The bottom panel shows the analogous phase on the (100) face of a simple cubic (single band) crystal, on which the calculations here are performed. The three trios have comparable strength (see fig. 3), suggesting that in the top panel the three dashed trios have strength comparable to the two solid trios and so there is no a priori reason to exclude them. This eases the required strength of trio repulsions needed to explain the phase diagram of O/W(110).

Theoretical investigations of adatom trio interactions are nonexistent, except for statements of the formal expression [12–14] and our brief explicit calculations of the moderately long-legged trios which occur within c(2 × 2) superlattices [13,14]. To gauge quickly how well the electronic indirect interaction picture accommodates CHLW's parameters, we extent this approach to a system which bears on O/W(110), namely single-level adatoms in bridge sites, σ-bonded [15] to the (001) face of single band simple cubic tight-binding substrate [16], as depicted in the lower part of fig. 1. The input parameters, listed in the caption of fig. 2, are representative of moderately strong covalent adsorption [13]. The adatom orbital might be viewed as the oxygen p_z, which is typically most lowered by adsorption [17,18]. Neither correlation effects [19] nor dipolar repulsions [20] are significant for our problem. From Liebsch's calculations of O/Ni(100) [17,18], we infer that overlap between p_z orbitals should not be very important here. However, overlap of $p_{x,y}$ orbitals probably does give a non-negligible direct contribution to the interaction
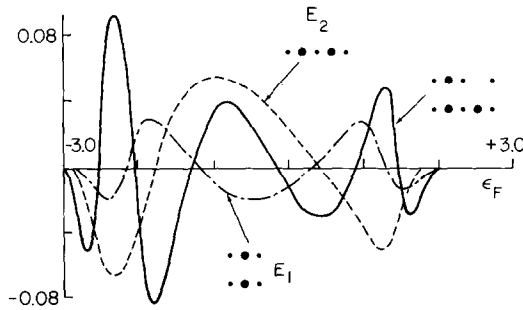
Fig. 2. The right-triangle trio interaction energy compared to *one-quarter* of the strongest pair interactions, E_1 and E_2. The energy unit is one-sixth the bandwidth and the center of the band the energy zero. (One would thus take this unit as 2eV here, although any numbers extracted from this model should be viewed in a qualitative way.) Adatom–substrate coupling is a σ-bond of moderate strength ($V_{eff} = 3/2$). The adatom is described by a single level near the center of the band ($\epsilon_a = -0.3$) [22]. In this case, the range over which E_1 and E_2 have the correct signs for p(2 × 1) structure is $-1 \lesssim \epsilon_F \lesssim 0$. Here the trio interaction does usually satisfy the criterion of ref. [6] (which is promulgated for a (110) case), that it be repulsive and greater than $| E_1 |/4$.

energies [21], both pair and trio, which should be considered in more detailed com-
putations. In this letter, we consider exclusively the indirect interaction via sub-
strate electron wavefunctions. Qualitatively, this trio interaction could be approxi-
mated by an electron making one traversal of the new triangular path in the sub-
strate, with hops at each corner to the adsorbate. There are significant semiquanti-
tative corrections, particularly from interference between the constituent pair inter-
actions [22].

Fig. 2 compares a trio interaction with *one-quarter* of the strongest pair inter-
actions. In this *particular* case, E_1 and E_2 are such that the (2 × 1) pattern would
arise only for $-1 \lesssim \epsilon_F \lesssim 0$, (but the upper limit does correspond to W in this
model). In this region, the trio interaction turns out to be repulsive as required,
although this could be an artifact of the input parameters. More significant is the
fact that it is usually greater than $|E_1|/4$, the criterion of CHLW. Since the (enve-
lope of the) pair interaction falls off as R^{-5} asymptotically (and faster for small R),
where R is the interadatom lateral separation [23–25], an increase of R by a factor
of $\sqrt{2}$ leads to a reduction of the average magnitude of the pair interaction energy
to at most 18% of the shorter R value; if R is doubled, the reduction is to 3%!
Thus, the magnitudes of the three trio interactions depicted should in general be
larger than any pair interactions except E_1 and E_2, though perhaps comparable to
the nearest diagonal pair [14].

    In fig. 3 are the trio interaction energies for the three configurations in which the
two shortest legs have the nearest-neighbor length. The curves have comparable
magnitudes but differences in details. The interaction is enhanced when two ada-
toms bond to the same substrate atom. This enhancement increases with adatom–
substrate coupling and was noted earlier for pair interactions when the adsorption
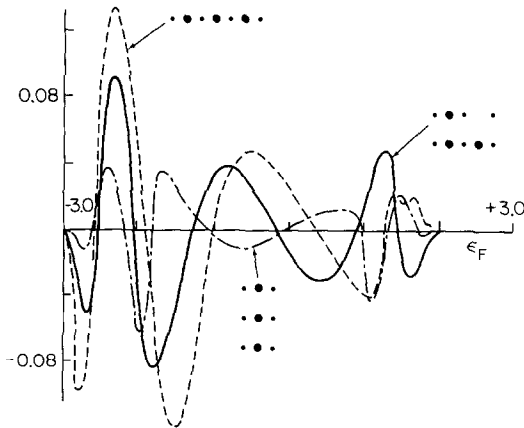
Fig. 3. Trio interaction energy versus substrate Fermi energy for the three trios in the lower panel of fig. 1. Again the abscissa is substrate band filling and the parameters are as in fig. 2. The curves are labeled by schematics of the relative orientation of the three adatoms.

was so strong as to produce states split off from the band [23]. The invariable negativity of the interaction near the bottom of the band (when there are no split-off states) as for the pair interaction [23], is a consequence of the long wavelength of the substrate eigenstates [25]. This figure indicates that the dashed triads in the upper part of fig. 1, neglected by CHLW, should have strengths comparable to the solid ones they included.

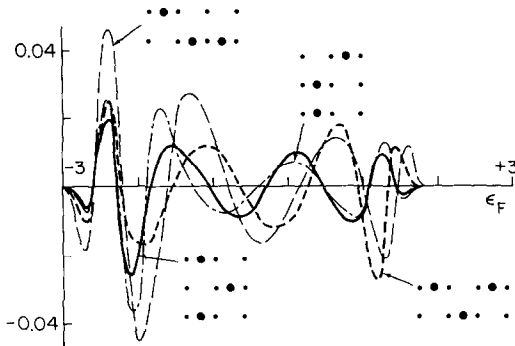To gauge how rapidly trio energies fall of with shortest-leg separation [22], we

Fig. 4. Trio interaction energies versus ϵ_F with the same parameters as the preceding figures. Two orientations of two types of adatom triangles with larger separations are plotted. The ordinate scale differs from that in figs. 2 and 3: these trio energies are substantially smaller than those in the preceding figures. For both the right triangles (heavy curves) and the obtuse triangles (light curves), the general magnitude of the trio interaction energy is insensitive to rotation relative to the substrate.

plot results for more configurations in fig. 4. These more widely separated triads have distinctly weaker interactions than those in fig. 3; those therefore presumably give the majority of any three-adatom effects. For both the right triangles and the obtuse triangles, the general magnitude of the interaction is insensitive to rotation relative to the substrate. This feature favors the contention that for O/W(110) if one includes the obtuse solid triangle of fig. 1, one should also include the obtuse dashed triangle [26].

All equations set down by CHLW are for zero temperature and thus could be obtained by counting occupied pair and trio configurations for the ordered adlayers at quarter, half, three-quarter, and full coverage. Our contention, that the dashed triads of fig. 1 should be included, can be incorporated into CHLW's equations and results remarkably easily. We find the following prescription for their parameters: (1) E_1 and E_2 should be augmented by the trio interaction energy of the diagonal and horizontal dashed linear triads, respectively; (2) the average value of the trio energy of the solid triads (CHLW's $\bar{E}_{TP}$) should be increased by the trio energy of the dashed obtuse triad [27]. This simple renormalization applies only to the ground state of the adatom system for ordered overlayers at the four given coverages. With the renormalized parameters indicated with tildas, CHLW's algebra carries through unchanged. The inequality $\tilde{\bar{E}}_{TP} > -\tilde{E}_1/4$ is now far easier to achieve. For illustration suppose all five triads in fig. 1 have trio energy E_T. Without renormalizing E_1, we find $E_T > -\tilde{E}_1/8$; including it gives $E_T > -E_1/9$. These "weakened" inequalities should be easily achievable by indirect interactions in real systems.

Comparisons of the ground state energies of the phases found in (and absent from) LEED-derived phase diagrams result in only inequalities between the lateral interaction energies. To produce actual values, one commonly fits the intensity (or the width) of the adlayer-induced LEED beams by Monte Carlo simulation, using the lateral energies as adjustable parameters. An important problem then is: what is the error in numbers derived from such fits when trio interactions are ignored? Fixing the attractive pair interactions and considering their two triad configurations, CHLW found $E_2 = 56$ meV and $\bar{E}_{TP} = 52$ meV; without these trios, they found $E_2 = 80$ meV, 43% too large. Now the normalization prescription for CHLW's trio parameter carries over to the random case [28], and so presumably is generally a reasonable approximation. Hence, with the obtuse dashed triad of fig. 1 added, the average trio energy should be halved without much further change in E_2. The role of the linear triads is less clear. In general, the amount by which E_1 and E_2 are renormalized should be some fraction of the appropriate linear trio energy; in the random limit this factor is just fractional coverage [28]. Even in this extreme limit, which should underestimate renormalization, the apparent pair energies for a (2×1) overlayer will include half the (average) trio energy. (Here E_2 would be 30% too large!)

For an ordered $c(2 \times 2)$ overlayer, we showed earlier [13,29] that the dominant pair interactions between (nearby) *occupied* sites could adequately describe the

general behavior of the lateral interaction per adatom. with quantitative agreement usually within a quarter. The *occupied* triads (corresponding to the linear configurations here) contributed about 10–30% of the (occupied) pair interaction(s). They were usually in the proper direction to explain the pair's shortfall in describing the complete overlayer interactions, sometimes overcompensating. The unoccupied triads, which only enter when thermal effects push adatoms into unfavorable lattice sites, were not considered in that study. As implied by CHLW, such trios will affect the fitting of the repulsive pair energies much more than attractive ones (especially at presaturated coverages).

In short, at current sophistication one should be skeptical of any Monte-Carlo-derived interaction energy given to more than one significant digit, and even that might often be only roughly valid. In addition to their qualitative role in causing phase diagram asymmetries, trio interactions will have substantial quantitative effects. There are many different interactions of comparable magnitude that must be included when considering low-symmetry systems. This problem heightens the need to calculate more than just LEED spot intensities in Monte Carlo simulations [7,9,14].

References

[1] G. Doyen, G. Ertl and M. Plancher, J. Chem. Phys. 62 (1975) 2957.
[2] K. Binder and D.P. Landau, Surface Sci. 61 (1976) 577;
    B. Mihura and D.P. Landau, Phys. Rev. Letters 38 (1977) 977.
[3] G. Ertl and D. Schillinger, J. Chem. Phys. 66 (1977) 2569.
[4] W.-Y. Ching, D.L. Huber, M. Fishkis and M.G. Lagally, J. Vacuum Sci. Technol. 15 (1978) 653.
[5] E.D. Williams, S.L. Cunningham and W.H. Weinberg, J. Vacuum Sci. Technol. 15 (1978) 417; J. Chem. Phys. 68 (1978) 4688.
[6] W.-Y. Ching, D.L. Huber, M.G. Lagally and G.-C. Wang, Surface Sci. 77 (1978) 550.
[7] L.D. Roelofs, R.L. Park and T.L. Einstein, J. Vacuum Sci. Technol. 16 (1979).
[8] With adsorption in the indicated bridge sites, E_1 and E_2 are decidedly not the same, so that it is reasonable that the pair interactions should differ so much. Since this is a (110)bcc face rather than a triangular lattice (e.g. (111)fcc), these pairs would be inequivalent even for adsorption in centered sites. (E.g. the separations of E_1 and E_2 pairs are $a\sqrt{3/2}$ and a, respectively.) However, it is unlikely that the band structure is sufficiently asymmetric for E_1 and E_2 to be so different if the adsorption were at centered sites. While M.A. Van Hove and S.Y. Tong, Phys. Rev. Letters 35 (1975) 1092 claimed adsorption does occur in three-fold centered sites, M.G. Lagally, J.C. Buchholz and G.-C. Wang, J. Vacuum Sci. Technol. 12 (1975) 213; M.G. Lagally, G.-C. Wang and T.-M. Lu, CRC Crit. Rev. Solid State Mater. Sci. 7 (1978) 233, using the method of constant momentum transfer aver-

aging, found results consistent with bridge bonding. Such a site is also more reasonable from a chemical point of view. M.G. Lagally, private communication.

[9] J.C. Buchholz and M.G. Lagally, Phys. Rev. Letters 35 (1975) 442; T.-M. Lu, G.-C. Wang and M.G. Lagally, Phys. Rev. Letters 39 (1977) 411; G.-C. Wang, T.-M. Lu and M.G. Lagally, to be published, discuss O/W(110).

[10] J. Behm, K. Christmann and G. Ertl, Solid State Commun. 25 (1978) 763, discuss H/Ni(111).

[11] P.J. Estrup, Phys. Today 28, No. 4 (1975) 33 and C.H. Huang, Ph.D. dissertation, Brown University (1974) discuss H/Mo(100) but surface reconstruction clouds the picture here and for H/W(100). R.A. Barker and P.J. Estrup, Phys. Rev. Letters 41 (1978) 1307.

[12] T.B. Grimley and S.M. Walker, Surface Sci. 14 (1969) 395.

[13] T.L. Einstein, in: Proc. 3rd Intern. Summer Inst. in Surface Science, Milwaukee, 1977; CRC Crit. Rev. Solid State Mater. Sci. 7 (1978) 261.

[14] T.L. Einstein, Surface Sci., to be published.

[15] We have also performed calculations for π-bonded adatoms. The magnitudes of interactions are comparable to σ-bonding, but the coupling is to the antisymmetric hybrid of the two substrate orbitals, shifting principal strength/activity of the interaction curves of figs. 2–4 to the upper half of the band. Cf., T.L. Einstein, Phys. Rev. B12 (1975) 1262 and ref. [23].

[16] D. Kalkstein and P. Soven, Surface Sci. 26 (1971) 85. P.E. Hunter and T.L. Einstein, unpublished, are considering the (110) face of a bcc lattice.

[17] A. Liebsch, Phys. Rev. Letters 38 (1977) 248.

[18] A. Liebsch, Phys. Rev. B17 (1978) 1653.

[19] K. Schönhammer, V. Hartung and W. Brenig, Z. Physik B22 (1975) 143.

[20] J.C. Tracy, Ph.D. dissertation, Cornell University (1969), gives a dipole moment per adatom of about a quarter debye. For the role of dipole–dipole interactions see, e.g., W. Kohn and K.H. Lau, Solid State Commun. 18 (1976) 553.

[21] When substantial, direct interaction can produce qualitative changes in adatom pair interactions. [N.R. Burke, Surface Sci. 58 (1976) 349.] In Leibsch's calculations for O/Ni(100) [17,18], he preliminary considered ordered two-dimensional square nets with nearest neighbor spacings of 3.52 and 2.49 Å for the c(2 × 2) and (1 × 1) cases, respectively. The resulting (two-dimensional) bandwidths give some idea of the magnitude of the overlaps; in a crude s-band tight-binding picture, the nearest-neighbor hopping is *one-eighth* this bandwidth. For the $p_{x,y}$ orbitals, this bandwidth is 1.5 and 4.5 eV for the c(2 × 2) and (1 × 1) cases, respectively; for the p_z orbital, it is 0.3 and 1.8 eV, respectively. For comparison, the interadatom distances appropriate to the E_1 and E_2 interactions on W(110) lie between the two Ni(100) numbers, at 2.74 and 3.16 Å, respectively; the adatom— substrate coupling we have selected for bridge bonding is slightly over 2 cV, far greater than any interadatom direct hopping parameter. Thus, direct interactions should not interfere with the pair indirect interactions between p_z orbitals; for the $p_{x,y}$ orbitals, the interadatom interaction probably contains a non-negligible direct component at the closest separations. Since all but one of the triads for O/W(110) contain a long leg, these interactions do require indirect coupling.

[22] Explicitly, we compute the interaction energy by integrating the phase shift, derived from the Fredholm determinant, of all occupied states as in refs. [12–14,23]. For the total lateral interaction of three adatoms, this determinant is $(1 - g_{12}^2 - g_{23}^2 - g_{12}^2 - 2g_{12}g_{23}g_{13})$, where $g_{ij}(\epsilon) \equiv V^2 \ [\epsilon - \epsilon_a - V^2 \ G_{ii}(\epsilon)]^{-1} \ G_{ij}(\epsilon)$ is the substrate propagator between sites i and j times the T matrix for hopping of between a substrate site and an adatom (with energy ϵ_a relative to the band center) coupled to it with strength V. To obtain the trio interaction, we must then subtract the three constituent pair energies, which are similar integrals, with determinant $(1 - g_{ij}^2)$. Ref. [23] indicates how to modify this

expression for bridge (rather than atop) bonding; V_{eff} is $V\sqrt{2}$ (cf. ref. [15]). In the triangular path approximation, one just integrates the phase shift due to $(l - 2g_{12}g_{23}g_{31})$, as though the pair terms cancelled out. Since this procedure essentially involves taking the natural logarithm of the determinant, a single traversal is the first-order term in the expansion of the ln. The factor of 2 corresponds to the possibility of clockwise or counterclockwise traversal of the triangular path. The pair interference term comes from subtracting the three pair interactions from an integral over phase shifts due to $(1 - g_{12}^2 - g_{23}^2 - g_{31}^2)$. A more detailed exposition is contained in the original version of this paper, available as Univ. of Maryland Tech. Rept. No. 79–077 (Physics Paper 79–106). This report also contains a fuller account of footnote [15], two additional figures, and an account of the asymptotic limit.

[23] T.L. Einstein and J.R. Schrieffer, Phys. Rev. B7 (1973) 3629.

[24] K.H. Lau and W. Kohn, Surface Sci. 75 (1978) 69.

[25] T.L. Einstein, Surface Sci. 75 (1978) 161L.

[26] Note, however, that the solid triangle is isosceles, while the dashed one is not quite, since the E_1 separation is 86.6% the E_2 separation. Cf. footnote [8].

[27] With scrutiny of fig. 1, it is not hard to verify these rules: For each instance in which both sites of an E_2 pair are occupied, the site immediately to, say, the right of the pair is also occupied, giving a contribution of the horizontal linear triad. The correspondence is one-to-one. Similar remarks apply for E_1. For each case in which all three sites of acute solid triangle are occupied, there is a single case of the nonlinear dashed triad being fully occupied, which one can see by translating the horizontal leg of the acute triangle one spacing to the right or left. Similar remarks apply to the obtuse solid triangle, but here the long leg must be rotated $90°$ (and shortened to a lattice spacing, of course).

[28] The contribution of a particular trio interaction to the free energy of the system must of course be multiplied by the correlation function of the associated product of three site operators in the lattice gas Hamiltonian. For saturated ordered adlayers, these are 0 or 1. In the high temperature (random) limit they all become θ^3, where θ is the fractional coverage. Since the correspondences detailed in the preceding footnote still hold, multiplying by θ^3 does not alter the prescription. On the other hand, in the random limit pair energies are multiplied by just θ^2, so that $\widetilde{E}_1$ and $\widetilde{E}_2$ are now formed from E_1 and E_2, respectively, by adding θ times the trio energy of the appropriate linear triad.

[29] T.L. Einstein, Phys. Rev. B16 (1977) 3411. T.B. Grimley and M.A. Rosales Medina, private communication, have performed a similar computation for the atop $c(2 \times 2)$ overlayer using a finer grid. While there are some minor changes (of order 10%) in some peak heights, the results are semiquantitatively similar.