The Long-Range Force between Chemisorbed Atoms

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> "There is now general agreement about the fact that forces between molecules are of electromagnetic origin and are due to the electromagnetic fields which surround such molecules, in their interaction with the charges in each of them and causing a distortion in their distribution. It is also clear that those interactions have to be described according to the rules of wave mechanics."
> P. DEBYE[1]

Abstract: The Hamiltonian operator for two hydrogen atoms chemisorbed on a metal is examined. The direct Coulomb interactions between the chemisorbed atoms are screened, and, as a result, indirect interactions *via* the conduction electrons in the metal become important. Three such couplings exist, but the long-range force is due to the sharing of electrons between a chemisorbed atom and the metal: one chemisorbed atom distorts the electron distribution in the metal; another interacts with this distortion.

The theoretical basis for a long-range interaction between two atoms chemisorbed on a metal has been known for some time,[2] but the quantitative treatment of the phenomenon is still in its early stages.[3] An investigation[3b] using a model Hamiltonian similar to that first used by Anderson[4] to treat magnetic impurities in simple metals shows that there is a long-range (inverse square) interaction energy between chemisorbed atoms which is oscillatory (attractive or repulsive depending on distance), nonisotropic, and dependent on the crystal face on which the atoms are chemisorbed. The range and the oscillatory character of the interaction are general consequences of the model Hamiltonian used, and, since this Hamiltonian is a very simple one, it is important to examine its validity. We shall show in this paper that this simple model Hamiltonian contains everything needed to describe correctly the *long-range* interaction between chemisorbed atoms. This is an important result. It does not, however, imply that the heat of chemisorption of an atom (or molecule) can be calculated with such a simple Hamiltonian. In the course of our discussion, we shall drop many terms which contribute to the heat but not to the interaction.

The Hamiltonian

We consider two hydrogen atoms A and B near a metal surface. The metal consists of ion cores with charges Ze at positions $\mathbf{R}_g$ and valency electrons. Let $\mathbf{R}_A$ and $\mathbf{R}_B$ denote the positions of the two protons, $\mathbf{r}_i$ that of the ith electron, and T_i its kinetic energy; then when the ion cores and the two protons are fixed, the Hamiltonian function is that given in eq 1. The last three terms describe the Coulomb interactions of the metal ion cores with one another, and with the two protons. We assume that the equilibrium positions of the metal ion cores do not change when the separation of the two chemisorbed atoms is changed. Consequently the last three terms in (1) do not contribute to the interaction between chemisorbed atoms, and we shall therefore drop them in what follows.

$$\mathcal{H} = \sum_i\left(T_i - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_A|} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_B|} - \sum_g \frac{Ze^2}{|\mathbf{r}_i - \mathbf{R}_g|}\right) + \frac{1}{2}\sum_{ij}{}' \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{e^2}{|\mathbf{R}_A - \mathbf{R}_B|} + \frac{1}{2}\sum_{gg'}{}' \frac{Ze^2}{|\mathbf{R}_g - \mathbf{R}_{g'}|} + \sum_g \frac{Ze^2}{|\mathbf{R}_A - \mathbf{R}_g|} + \sum_g \frac{Ze^2}{|\mathbf{R}_B - \mathbf{R}_g|} \quad (1)$$

We write the quantum mechanical operator corresponding to (1) in the language of second quantization because we wish to approximate the Hamiltonian operator itself, not its wave functions. Following Anderson[4] we choose a representation consisting of a set of spin orbitals $\phi_{\mathbf{k}\sigma}$ for electrons in the conduction band of the metal, and the 1s atomic spin orbitals $\phi_{A\sigma}$ and $\phi_{B\sigma}$ for electrons in the two hydrogen atoms. σ specifies the spin, and is either ↑ or ↓, but to make our formulas less cumbersome we often contract $\mathbf{k}\sigma$ to the single symbol $\mathbf{k}$, and we use ϕ_F or ϕ_G to denote *any* atomic spin orbital.

The atomic orbitals ϕ_A and ϕ_B are orthogonal only when $|\mathbf{R}_A - \mathbf{R}_B|$ is large, so choosing our representation in this way restricts us at the outset to a discussion of the long-range interaction between chemisorbed atoms. This restriction can be avoided if ϕ_A and ϕ_B are replaced by the $1\sigma_g$ and $1\sigma_u$ molecular orbitals of either H_2 or H_2^+, but we shall not pursue this here. The conduction band orbitals $\phi_\mathbf{k}$ are not eigenfunctions of the ion core potential $-\Sigma_g Ze^2/|\mathbf{r} - \mathbf{R}_g|$; they are eigenfunctions of a certain self-consistent crystal potential, *e.g.*, V_{cp}. The details of this crystal potential will not concern us at present.

In the formalism of second quantization, every spin orbital $\phi_{\mu\sigma}$ (μ = $\mathbf{k}$, A or B) has associated with it creation, destruction, and number operators, $c_{\mu\sigma}^+$, $c_{\mu\sigma}$, and $n_{\mu\sigma}$, respectively, and the Hamiltonian operator is a function of these operators. Dropping the last

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(1) From his summary of the anticipated contents of the Study Week on Molecular Forces, organized by the Pontifical Academy of Science, and held in Vatican City in April 1966.

(2) (a) T. B. Grimley, "Chemisorption," W. E. Garner, Ed., Butterworth and Co. Ltd., London, 1956, p 26; (b) J. Koutecký, *Trans. Faraday Soc.*, **54**, 1038 (1958).

(3) (a) T. B. Grimley, Pontificiae Academiae Scientiarum Scripta Varia n. 31, Study Week on The Molecular Forces, Vatican City, 18–23 April 1966; (b) T. B. Grimley, *Proc. Phys. Soc.*, **90**, 751 (1967).

(4) P. W. Anderson, *Phys. Rev.*, **124**, 41 (1961).

three terms in (1) and remembering that $|\mathbf{R}_A - \mathbf{R}_B|$ is large so that ϕ_A and ϕ_B do not overlap, the result is eq 2. Here E is the 1s orbital energy of hydrogen, and

$$H = (E + x)\sum_{F} n_F + \sum_{\mathbf{k}}(\epsilon_{\mathbf{k}} + x_{\mathbf{kk}})n_{\mathbf{k}} + U(n_{A\uparrow}n_{A\downarrow} + n_{B\uparrow}n_{B\downarrow}) + H_{\text{mix}} + H_s + \Delta H + H_c + \frac{e^2}{|\mathbf{R}_A - \mathbf{R}_B|} \quad (2)$$

the orbital energies of electrons in the conduction band of the metal are $\epsilon_{\mathbf{k}}$.

$$x = -\left\langle A \left| \frac{e^2}{|\mathbf{r} - \mathbf{R}_B|} + \sum_{g} \frac{Ze^2}{|\mathbf{r} - \mathbf{R}_g|} \right| A \right\rangle \quad (3)$$

is the shift of the 1s energy of atom A in the field of proton B and the metal ion cores

$$x_{\mathbf{kl}} = -\left\langle \mathbf{k} \left| \frac{e^2}{|\mathbf{r} - \mathbf{R}_A|} + \frac{e^2}{|\mathbf{r} - \mathbf{R}_B|} \right| \mathbf{l} \right\rangle \quad (4)$$

so that $x_{\mathbf{kk}}$ is the energy shift of the conduction band state $\phi_{\mathbf{k}}$ in the field of the two protons on the surface of the metal. H_{mix} describes the sharing of the electrons between the metal and the chemisorbed atoms (eq 5), where T is the kinetic energy operator. H_{mix}

$$H_{\text{mix}} = \sum_{F\mathbf{k}}(V_{F\mathbf{k}}c_F{}^+c_{\mathbf{k}} + V_{\mathbf{k}F}c_{\mathbf{k}}{}^+c_F)$$

$$V_{F\mathbf{k}} = \left\langle F \left| T - \frac{e^2}{|\mathbf{r} - \mathbf{R}_A|} - \frac{e^2}{|\mathbf{r} - \mathbf{R}_B|} - \sum_{g} \frac{Ze^2}{|\mathbf{r} - \mathbf{R}_g|} \right| \mathbf{k} \right\rangle \quad (5)$$

gives rise to the $|\mathbf{R}_A - \mathbf{R}_B|^{-2}$ interaction referred to in the introductory section. H_s, defined by (6), describes a

$$H_s = \sum_{\mathbf{kl}}{}' x_{\mathbf{kl}}c_{\mathbf{k}}{}^+c_{\mathbf{l}} \quad (6)$$

scattering of the conduction band states by the two protons, and, as we shall see later, leads to an interaction between the chemisorbed atoms. The term

$$\Delta H = -\sum_{\mathbf{kl}}\left\langle \mathbf{k} \left| \sum_{g} \frac{Ze^2}{|\mathbf{r} - \mathbf{R}_g|} + V_{\text{cp}} \right| \mathbf{l} \right\rangle \quad (7)$$

is present because the states $\phi_{\mathbf{k}}$ are not eigenfunctions of the ion core potential but of V_{cp}, but we shall see later that ΔH is cancelled by some of the terms in H_c. All Coulomb interactions of electrons in the metal with one another, and with electrons in the chemisorbed atoms as well as the Coulomb interactions of electrons in atom A with those in B, are contained in H_c; the Coulomb interactions between electrons in the *same* chemisorbed atom A or B are written explicitly (the third term) in (2). H_c has ten terms (eq 7′). The four

$$\begin{aligned} H_c = {} & \frac{1}{2}\sum_{\mathbf{klmn}} Q_{\mathbf{klmn}}c_{\mathbf{k}}{}^+c_{\mathbf{l}}{}^+c_{\mathbf{n}}c_{\mathbf{m}} + \sum_{\mathbf{klm}F}(Q_{F\mathbf{klm}}c_F{}^+c_{\mathbf{k}}{}^+c_{\mathbf{m}}c_{\mathbf{l}} + \\ & Q_{\mathbf{kl}F\mathbf{m}}c_{\mathbf{k}}{}^+c_{\mathbf{l}}{}^+c_{\mathbf{m}}c_F) + \frac{1}{2}\sum_{\mathbf{kl}FG}(Q_{FG\mathbf{kl}}c_F{}^+c_G{}^+c_{\mathbf{l}}c_{\mathbf{k}} + \\ & Q_{\mathbf{kl}FG}c_{\mathbf{k}}{}^+c_{\mathbf{l}}{}^+c_Gc_F) + \sum_{\mathbf{kl}F} Q_{F\mathbf{k}F\mathbf{l}}n_Fc_{\mathbf{k}}{}^+c_{\mathbf{l}} + \\ & \sum_{\mathbf{kl}FG} Q_{F\mathbf{kl}G}c_F{}^+c_{\mathbf{k}}{}^+c_Gc_{\mathbf{l}} + \sum_{\mathbf{k}FG}(Q_{\mathbf{k}FGF}n_Fc_{\mathbf{k}}{}^+c_G + \\ & Q_{FG\mathbf{k}G}c_F{}^+c_{\mathbf{k}}n_G) + \frac{1}{2}\sum_{\sigma\sigma'} Q_{A\sigma B\sigma' A\sigma B\sigma'}n_{A\sigma}n_{B\sigma'} \end{aligned} \quad (7')$$

index symbols like $Q_{\mathbf{klmn}}$, for example, stand for the matrix elements of the electron interaction

$$Q_{\mathbf{klmn}} = \left\langle \mathbf{kl} \left| \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \mathbf{mn} \right\rangle$$

and the quantity U in (2) is $Q_{A\uparrow A\downarrow A\uparrow A\downarrow}$. Finally the last term in (2) is the Coulomb repulsion of the two protons.

Of course the Coulomb terms H_c make the Hamiltonian (2) very difficult to handle, but they play an essential role in our problem because they *shield* many of the simpler terms in H.

Screening and Shielding

The terms

$$\sum_{\mathbf{k}} x_{\mathbf{kk}}n_{\mathbf{k}} + H_s \quad (8)$$

in H describe the perturbation of the conduction band electrons by the two protons on the metal surface. This perturbation induces a change in the electron density in the metal near the two protons, and as a result the electrical potential of the two protons is *screened.* If we ignore H_c, in particular the first term which describes the Coulomb interactions of the electrons in the metal, the screening charge induced in the metal by each proton turns out to be infinite. This is wrong, of course; the first term in H_c cannot be ignored because it responds to the perturbation 8. Through this response, the effect of perturbation 8 on the system is *shielded,* and the screening charge induced by each proton is reduced to one electronic charge. The final situation is that, by screening, the long-range Coulomb potential of each proton is changed in the metal into a short-range screened potential which is generally nonisotropic. Thus

$$-\frac{e^2}{|\mathbf{r} - \mathbf{R}_A|} - \frac{e^2}{|\mathbf{r} - \mathbf{R}_B|} \longrightarrow w(\mathbf{r} - \mathbf{R}_A) + w(\mathbf{r} - \mathbf{R}_B) \quad (9)$$

and the energy shifts $x_{\mathbf{kk}}$ and the quantities $x_{\mathbf{kl}}$ in H_s become matrix elements of a potential which is localized near the two protons A and B (eq 10); we notice

$$\begin{gathered} x_{\mathbf{kk}} \longrightarrow \Delta\epsilon_{\mathbf{k}} = 2w_{\mathbf{kk}}(0) \\ x_{\mathbf{kl}} \longrightarrow w_{\mathbf{kl}}(\mathbf{R}_A) + w_{\mathbf{kl}}(\mathbf{R}_B) \\ w_{\mathbf{kl}}(\mathbf{R}) = \langle \mathbf{k}|w(\mathbf{r} - \mathbf{R})|\mathbf{l}\rangle \end{gathered} \quad (10)$$

that the level shift, which we now call $\Delta\epsilon_{\mathbf{k}}$, is independent of $\mathbf{R}_A$ and $\mathbf{R}_B$.

When $|\mathbf{R}_A - \mathbf{R}_B|$ is large, it is clear that, seen from A, proton B and its induced screening charge in the metal appear as an electric dipole. Consequently, a second effect of the screening charges is to change the $e^2/|\mathbf{R}_A - \mathbf{R}_B|$ repulsion of the two protons into an interaction which, for large values of $|\mathbf{R}_A - \mathbf{R}_B|$, becomes a dipole–dipole repulsion varying as $|\mathbf{R}_A - \mathbf{R}_B|^{-3}$. Similarly the 1s energy level shift of eq 3 is changed.

$$x \longrightarrow \Delta E = -\left\langle A \left| \sum_{g} \frac{Ze^2}{|\mathbf{r} - \mathbf{R}_g|} \right| A \right\rangle + O(|\mathbf{R}_A - \mathbf{R}_B|^{-3}) \quad (11)$$

The changes expressed in (10) and (11) involve the Coulomb terms H_c only indirectly as a result of the response of these terms to a perturbation. However, the Coulomb terms have important direct effects, and we now examine these.

The first term in H_c describes the Coulomb interactions between electrons in the metal, and it is well known that these interactions are screened. In any case this term has no explicit dependence on $\mathbf{R}_A$ and $\mathbf{R}_B$, and because of this it does not cause any serious difficulty in our problem. Its important direct effect is to cancel ΔH in (2). To see this we put either $\mathbf{n} = \mathbf{k}$ or l or $\mathbf{m} = \mathbf{k}$ or l so as to get a number operator and the product of two Fermion operators. This gives the term

$$\sum_{\mathbf{klm}}(Q_{\mathbf{kmlm}} - Q_{\mathbf{kmml}})n_{\mathbf{m}}c_{\mathbf{k}}^{+}c_{\mathbf{l}} \qquad (12)$$

and if we now make an approximation by replacing the number operator by its expectation value in the ground state of the unperturbed metal, the coefficient of $c_{\mathbf{k}}^{+}c_{\mathbf{l}}$ in (12) becomes the **kl** matrix element of the Coulomb and exchange potential acting on an electron in the unperturbed metal. But this potential, when added to the ion core potential, gives the self-consistent crystal potential V_{cp} in (7). Hence the term 12 cancels ΔH in (2).

The other nine terms in H_c involve one, or both, of the positions $\mathbf{R}_A$ and $\mathbf{R}_B$ explicitly, and since these terms cannot be handled exactly, we shall have to make an approximation if we are to discuss their effects. The approximation we make is the same as that already made in connection with (12); namely, we only retain those four-Fermion terms which are the product of two Fermion operators and a number operator, and we replace the number operator by its expectation value in the Hartree–Fock ground state. Thus from the second and third terms in H_c we only retain

$$\sum_{\mathbf{kl}F}\{(Q_{F\mathbf{lkl}} + Q_{F\mathbf{llk}})n_{\mathbf{l}}c_F^{+}c_{\mathbf{k}} + (Q_{\mathbf{kl}F\mathbf{l}} - Q_{\mathbf{lk}F\mathbf{l}})n_{\mathbf{l}}c_{\mathbf{k}}^{+}c_F\}$$

and adding this to the eighth and ninth terms in H_c we find, after replacing number operators by their expectation values, a contribution to H which has the same form as H_{mix} in (5) but with $V_{F\mathbf{k}}$ replaced by

$$\sum_{\mathbf{l}}(Q_{F\mathbf{lkl}} - Q_{F\mathbf{llk}})n_{\mathbf{l}} + \sum_{G \neq F} Q_{FG\mathbf{k}G}n_G \qquad (13)$$

But expression 13 is the **Fk** matrix element of the Coulomb and exchange potential experienced by an electron in the system metal plus chemisorbed atoms in the Hartree–Fock ground state. Consequently the direct effect of these Coulomb terms is to change the meaning of $V_{F\mathbf{k}}$ in (5) so that

$$V_{F\mathbf{k}} \longrightarrow \langle F|T + V_{SCF}|\mathbf{k}\rangle \qquad (14)$$

where V_{SCF} is the potential energy operator for an electron in the Hartree–Fock self-consistent field of the system.

The fourth and fifth terms in H_c make no contribution to H in our present approximation. The sixth and seventh terms contribute

$$\sum_{\mathbf{k}F}(Q_{F\mathbf{k}F\mathbf{k}} - Q_{F\mathbf{kk}F})n_F n_{\mathbf{k}} + \\ \sum_{\substack{\mathbf{kl}F \\ (\mathbf{k} \neq \mathbf{l})}}(Q_{F\mathbf{k}F\mathbf{l}} - Q_{F\mathbf{kl}F})n_F c_{\mathbf{k}}^{+}c_{\mathbf{l}} - \sum_{\mathbf{k}FG} Q_{F\mathbf{kk}G}n_{\mathbf{k}}c_F^{+}c_G \qquad (15)$$

The first term in (15) will, after replacing $n_{\mathbf{k}}$ by its expectation value, correct the 1s level shift ΔE for the Coulomb and exchange interaction of the electrons in the chemisorbed atom with those in the metal. In the second term we replace n_F by its expectation value to get a contribution with the same form as H_s in (6) but with the **kl** matrix element of the Coulomb and exchange potential of the electrons in the chemisorbed hydrogen atoms replacing that of the Coulomb potential of the protons. We have seen that the latter is *screened* in the metal, and the Coulomb and exchange potential of the atomic electrons will be screened in the same way. Consequently, although the exact definition of the matrix elements $x_{\mathbf{kl}}$ in H_s is changed by these terms in H_c, the general conclusion that they are matrix elements of a potential which is localized near the two protons is not altered, and this is important in our present problem. The third term in (15) is an important contribution to H, and we consider it in detail later.

The tenth term in H_c is the Coulomb interaction of the electrons in one chemisorbed atom with those in the other, but an electron localized on a chemisorbed atom induces screening charges in the metal (through the sixth term in H_c) which change this Coulomb interaction of the electrons, just as that of the two protons is changed, into a repulsion varying as $|\mathbf{R}_A - \mathbf{R}_B|^{-3}$ when $|\mathbf{R}_A - \mathbf{R}_B|$ is large.

Taking all the above modifications into account, formula 2 for H now becomes eq 16.

$$H = (E + \Delta E)\sum_{\sigma}(n_{A\sigma} + n_{B\sigma}) + \sum_{\mathbf{k}\sigma}(\epsilon_{\mathbf{k}} + \Delta\epsilon_{\mathbf{k}})n_{\mathbf{k}\sigma} + \\ U(n_{A\uparrow}n_{A\downarrow} + n_{B\uparrow}n_{B\downarrow}) + H_{\text{mix}} + H_s + \\ H_{\text{ex}} + H_c' + O(|\mathbf{R}_A - \mathbf{R}_B|^{-3}) \qquad (16)$$

H_{mix} is defined by (5) but with $V_{F\mathbf{k}}$ changed in accordance with (14), and

$$H_s = \sum_{\mathbf{kl}}{}'\{w_{\mathbf{kl}}(\mathbf{R}_A) + w_{\mathbf{kl}}(\mathbf{R}_B)\}c_{\mathbf{k}}^{+}c_{\mathbf{l}} \qquad (17)$$

with $w_{\mathbf{kl}}(\mathbf{R}_A)$ the **kl** matrix element of a short-range potential localized on atom A, and $w_{\mathbf{kl}}(\mathbf{R}_B)$ the same for atom B

$$H_{\text{ex}} = -\sum_{\sigma}(J_{AB}\,c_{A\sigma}^{+}c_{B\sigma} + J_{BA}c_{B\sigma}^{+}c_{A\sigma}) \\ J_{AB} = \sum_{\mathbf{k}} Q_{A\sigma\mathbf{k}\sigma\mathbf{k}\sigma B\sigma}\,n_{\mathbf{k}\sigma} \qquad (18)$$

and H_{ex} is an indirect interaction of the two chemisorbed atoms *via* the exchange interaction of their electrons with the electrons in the conduction band of the metal. Finally H_c' contains all those Coulomb terms whose effects are not included either in the screening and shielding discussed in this section, or in the self-consistent potential V_{SCF}. The principal effect of these terms is to shield H_{mix}, H_s, and H_{ex} in the sense that they alter the exact definitions of $V_{F\mathbf{k}}$, $w_{\mathbf{kl}}$, and J_{AB}. We shall not therefore consider them in detail. We have indicated in (16) that terms asymptotically proportional to $|\mathbf{R}_A - \mathbf{R}_B|^{-3}$ have been dropped. It is important to remember this.

Indirect Interactions

The interaction between two chemisorbed atoms arising from the term H_{mix} in (16) has already been examined in detail.[3b] The interaction energy is oscillatory but falls off like $|\mathbf{R}_A - \mathbf{R}_B|^{-2}$. We shall now derive the asymptotic forms of the interactions arising from H_s and H_{ex}. We can use perturbation theory for this taking the first three terms in (16) as the unperturbed Hamiltonian; both terms contribute separately to the interaction in second order. The interaction energy from H_s is

$$W_s = 2\sum_{\substack{\mathbf{l} > \mathbf{k}_F \\ \mathbf{k} < \mathbf{k}_F}} w_{\mathbf{kl}}(\mathbf{R}_A) w_{\mathbf{lk}}(\mathbf{R}_B)/(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{l}}) \tag{19}$$

where $\mathbf{k}_F$ defines the Fermi level, and that from H_{ex} is

$$W_{ex} = -4|J_{AB}|^2/U \tag{20}$$

W_{ex} actually stabilizes an antiparallel alignment of spins on the chemisorbed atoms, but this aspect of H_{ex} will not detain us here.

To evaluate the matrix elements in (19) and (20) we expand the conduction band wave functions $\phi_{\mathbf{k}}$ in terms of the point Wannier functions $a(\mathbf{r} - \mathbf{R}_g)$ centered on the lattice points $\mathbf{R}_g$ of the semiinfinite metal

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_g U(\mathbf{k}, \mathbf{R}_g) a(\mathbf{r} - \mathbf{R}_g) \tag{21}$$

Since $w(\mathbf{r} - \mathbf{R}_A)$ is a short-range potential, the main contribution to $w_{\mathbf{kl}}(\mathbf{R}_A)$ comes from the Wannier function on the lattice point, $\mathbf{R}_0$ say, over which atom A is adsorbed. Hence

$$w_{\mathbf{kl}}(\mathbf{R}_A) \simeq wU^*(\mathbf{k}, \mathbf{R}_0)U(\mathbf{l}, \mathbf{R}_0)$$

where w is independent of $\mathbf{k}$ and $\mathbf{l}$.

The periodicity of a semiinfinite metal is described by only two primitive translations which depend on the surface plane, and which define a two-dimensional subspace of the usual $\mathbf{k}$ space. If $\mathbf{k}'$ is a vector lying in this subspace then, because $\mathbf{R}_B - \mathbf{R}_A$ lies in the surface

$$\phi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_B - \mathbf{R}_A) = \exp\{i\mathbf{k}'\cdot(\mathbf{R}_B - \mathbf{R}_A)\}\phi_{\mathbf{k}}(\mathbf{r}) \tag{22}$$

Consequently $w_{\mathbf{lk}}(\mathbf{R}_B)$ and $w_{\mathbf{lk}}(\mathbf{R}_A)$ are related

$$w_{\mathbf{lk}}(\mathbf{R}_B) = \exp\{i(\mathbf{l}' - \mathbf{k}')\cdot(\mathbf{R}_B - \mathbf{R}_A)\} w_{\mathbf{kl}}(\mathbf{R}_A)$$

and hence

$$w_{\mathbf{kl}}(\mathbf{R}_A) w_{\mathbf{lk}}(\mathbf{R}_B) \simeq |wU(\mathbf{k},\mathbf{R}_0)U(\mathbf{l},\mathbf{R}_0)|^2 \exp\{i(\mathbf{l}' - \mathbf{k}')\cdot(\mathbf{R}_B - \mathbf{R}_A)\}$$

If we substitute this into (19), ignore the dependence of $U(\mathbf{k},\mathbf{R}_0)$ on $\mathbf{k}$, and assume a free-electron energy spectrum for electrons in the conduction band, the right-hand side of (19) is easily evaluated.[5] The result is that W_s has the range factor $F(2k_F|\mathbf{R}_A - \mathbf{R}_B|)$, where

$$F(x) = (x \cos x - \sin x)/x^4$$

Hence W_s falls off like $|\mathbf{R}_A - \mathbf{R}_B|^{-3}$, and since we have already dropped terms of this sort in arriving at (16), it is now clear that we cannot retain H_s either.

To evaluate J_{AB} in (18) we again use (21) and (22) and assume that the main contribution comes from the Wannier functions on the lattice points over which the atoms A and B are adsorbed. Thus

$$Q_{A\sigma\mathbf{k}\sigma\mathbf{k}\sigma B\sigma} \simeq |vU(\mathbf{k},\mathbf{R}_0)|^2 \exp\{i\mathbf{k}'\cdot(\mathbf{R}_B - \mathbf{R}_A)\}$$

where v is independent of $\mathbf{k}$. Treating the conduction band electrons as free and ignoring the $\mathbf{k}$ dependence of $U(\mathbf{k},\mathbf{R}_0)$, we now find that

$$J_{AB} \propto 2k_F|\mathbf{R}_A - \mathbf{R}_B|F(2k_F|\mathbf{R}_A - \mathbf{R}_B|)$$

Hence J_{AB} falls off like $|\mathbf{R}_A - \mathbf{R}_B|^{-2}$, and from (20) this means that W_{ex} falls off like $|\mathbf{R}_A - \mathbf{R}_B|^{-4}$. Consequently H_{ex} cannot be retained in (16). This leaves only H_{mix} and the Coulomb terms H_c' to provide a coupling between the chemisorbed atoms. We recall that H_{mix} gives rise to an interaction W_{mix} which falls off like $|\mathbf{R}_A - \mathbf{R}_B|^{-2}$, and we have now verified that there are no interactions having a longer range than this. With perturbation theory we would have to go to fourth order to calculate W_{mix} because H_{mix} is a typical "field-particle " interaction,[3a] but W_{mix} can in fact be evaluated without using perturbation theory.[3b] We note that none of the Coulomb terms in H_c' will commute with H_{mix}, and therefore they all contribute to its shielding. The calculation of the shielded matrix elements which replace $V_{F\mathbf{k}}$ in H_{mix} is an important problem for future work.

Although W_{mix} has the longest range of all the interactions between chemisorbed atoms, its magnitude could be so small as to be physically insignificant so that in practice one of the shorter range interactions is dominant. In particular, it might be that the ordinary dipole–dipole interaction between chemisorbed atoms, which comes from the terms asymptotically proportional to $|\mathbf{R}_A - \mathbf{R}_B|^{-3}$ in the Hamiltonian (16), is really the important long-range interaction, not W_{mix} or any other indirect interaction. To examine this point suppose that the dipole moment associated with a chemisorbed atom and its screening charge in the metal is 1 Debye. Then W_{dd}, the interaction energy of two such dipoles separated by a distance R, is given by

$$W_{dd} = \frac{2 \times 10^{-12}}{R^3} \text{ erg}$$

when R is measured in angstroms. To estimate W_{mix} we use eq 44 of ref 3b. For hydrogen on tungsten we take $U = 17$ ev and $\epsilon_F = 7.5$ eV so that $q_F = 1.40 \times 10^8$ cm^{-1}. Then with $q_F r_0 = q_F b = 1$, we find

$$W_{mix} = \left(\frac{4.8 \times 10^{-12}}{R^2}\right) \sin (2.8R) \text{ erg}$$

Consequently W_{mix} is indeed a physically significant long-range interaction, and it dominates W_{dd} when R is greater than about 0.5 Å.

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[5] See *e.g.*, C. Kittel, "Quantum Theory of Solids," John Wiley and Sons, Inc., New York, N. Y., 1963, p 364.