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PHYSICAL REVIEW B

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## Pseudopotential for the Calculation of Transition Rates of Atoms Chemisorbed on Metals\*

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We isolate the part of the interaction responsible for energy transfers between reacting chemicals adsorbed on a solid from the part that gives the potential-energy surface familiar in the description of the bonding of adsorbates.

### I. INTRODUCTION

Chemical reactions are generally described by rate equations. If the reaction is of the so-called "adiabatic" kind, these are differential equations for the numbers of the various participating species which, at a given time after the onset of the reaction, find themselves in the various quasistationary energy levels appropriate to the various wells of the energy surface calculated by assigning fixed values to the core coordinates, neglecting the core kinetic energy, and solving the Schrödinger equation for the motion of the outer electrons. The energy so calculated is a function of the core coordinates. It is represented by a hypersurface in the space of these coordinates and acts as potential energy in the next stage of a so-called Born-Oppenheimer calculation of the motion of the cores.

A reaction corresponds to the transfer of the system from one minimum on the hypersurface to another, via a saddlepoint. Quantum mechanically the process can be described by a rate equation describing the occupation numbers of the various (quasistationary) levels in the minima as a function of the time.<sup>1</sup> Its solution generally leads to a reaction-rate formula of the type given by Eyring *et al.*<sup>2</sup>

The general problem of the establishment of rate equations was discussed by Van Hove,<sup>3</sup> who noted that special care is required when the Hamiltonian of the system does not obviously split into an unperturbed part and an extremely small perturbation. Other criteria then determine the decomposition.

This question is especially acute in the case of chemical reactions. The same forces that mold the effective potential well in which the reagents find themselves are presumably also the forces responsible for the reaction. We here focus attention on the case in which some or all of the reagents are chemisorbed on the surface of a metal.

This metal substrate is approximated, for simplicity, by a semi-infinite uniform fixed background of positive charge pervaded by conduction electrons. This approximation precludes phonon processes in the reaction and focuses attention on the effects of electron charge and spin fluctuations as the operative dynamic factor in the reactions of chemisorbed species. Generalization to the case in which phonons, too, are operative is not difficult, however.

In searching for a "small" perturbation for use in the calculation of the transition coefficients that occur in the rate equation, one must clearly go beyond the straightforward expression for the interaction of the adatoms with the metal. That interaction is responsible for the very level scheme within which it induces transitions, and is thus hardly to be regarded as perturbation.

The appropriate decomposition of the Hamiltonian into a perturbed and unperturbed part is determined by a physical hypothesis as to which variables in the problem are slowly varying. For example, it is reasonable to suppose, at least in some cases, that the nuclear motion of the adatoms, as governed by the level scheme of the Born-Oppenheimer well, is described by level occupation numbers that change slowly compared with the rate of charge or

spin fluctuations of the electron gas. The "unperturbed" Hamiltonian will be that part  $\mathcal{H}$  of  $H$  which commutes with all such slowly varying quantities, and the perturbation will be  $\mathcal{U} = H - \mathcal{H}$ . An expression for  $\mathcal{U}$  somewhat reminiscent of that of pseudopotential theory in band-structure calculations can be derived by a consideration of the probable form of the spectrum of  $H$ .

## II. ENERGY SPECTRUM OF TOTAL SYSTEM

In an isolated reasonably small molecule, there is one energy function  $E_i(\vec{R})$  for each electronic eigenstate calculated for a fixed core configuration (here  $\vec{R}$  stands for all the nuclear coordinates). In most cases, the separation between different  $E_i$ 's is of the order of a volt or volts. When there is a metal substrate, the gaps between successive  $E_i$ 's are filled with a continuum of excitations, and so the  $E_i$ 's lose their precise meaning. However, let  $E_0(\vec{R})$  be the ground-state energy. This  $E_0(\vec{R})$  acts as an effective potential well for the adatom cores, and there will be one continuum sequence of excitations for which the shape of this well does not change materially. At an excitation energy of a volt or so, an additional continuum sequence will begin, with a quite different well shape [corresponding to  $E_1(\vec{R})$ ], and so on. Here we restrict ourselves to the first class of excitations. The well shape is insensitive to these excitations since they are described by wave functions characteristic of the infinite substrate, either in the sense of wave packets remote from the adsorption sites, or in the sense of plane waves extending everywhere, but with amplitudes of order  $1/\text{volume}^{1/2}$ , and correspondingly small overlap with the adatom. This suggests that the exact energies (for fixed  $\vec{R}$ ) in this first spectral series be written in the form

$$E(\vec{R}, \epsilon) = E_0(\vec{R}) + \epsilon - \epsilon_0 + \delta E(\vec{R}, \epsilon), \quad (1)$$

where  $E_0(\vec{R})$  is the exact ground-state energy of the total system,  $\epsilon_0$  the exact ground-state energy of the pure semi-infinite substrate,  $\epsilon$  one of its excitation energies, and  $\delta E(\vec{R}, \epsilon)$  a small energy shift. In general,  $\delta E$  and  $E$  will not only be a function of  $\vec{R}$  and  $\epsilon$ , but also a function of other quantum numbers of the substrate, depending on exactly which of the many states of energy  $\epsilon$  is under consideration. At first glance,  $\delta E$  would seem to be of order of the reciprocal volume. However, this is questionable in view of recent work on the so-called infrared catastrophe in the response of an electron gas to a fixed potential.<sup>4</sup> As should be evident, we are planning to use an operator representation of  $\delta E$  as a kind of perturbation, and we shall suppose that the problem of the infrared catastrophe is resolved either through nonadiabatic recoil effects, or, even if these are neglected, as the result of integrability in the final sum over

electron states.

## III. DECOMPOSITION OF HAMILTONIAN

Next we must find the unperturbed Hamiltonian, that is to say, the Hamiltonian whose eigenvalues are

$$E = E_0(\vec{R}) + \epsilon - \epsilon_0. \quad (2)$$

Let  $|0\rangle$  be the exact ground state of the total system. Consider the eigenstates  $|\epsilon\rangle$  of the substrate, with only the adatom cores *but not their outer electrons* removed from the scene. (Thus, for the present, the substrate is negatively ionized.)

Then the states

$$|\epsilon'\rangle = |\epsilon\rangle - |0\rangle\langle 0|\epsilon\rangle \quad (3)$$

are orthogonal to  $|0\rangle$ , but not among themselves. However, they can be orthogonalized, and in such a way that the order of the labeling  $\epsilon$  is preserved. Let  $\{\epsilon\}$  be the complete orthonormal set formed in this way, the state  $\{\epsilon_0\}$  (derived from  $|\epsilon_0\rangle$ , the ground state of the substrate alone) being omitted. Consider

$$\mathcal{H} = |0\rangle E_0(\vec{R}) \langle 0| + \sum_{\epsilon \neq \epsilon_0} \{\epsilon\} [\epsilon + E_0(\vec{R}) - \epsilon_0] \langle \epsilon|. \quad (4)$$

The eigenstates of  $\mathcal{H}$  are  $(|0\rangle, \{\epsilon\})$  with eigenvalues precisely given by the set (2). The perturbation to be used for working out the transition coefficients in the rate equation<sup>3</sup> is now  $\mathcal{U} = H - \mathcal{H}$ . Since  $H_0 = \sum |\epsilon\rangle \epsilon \langle \epsilon|$  (including the term  $\epsilon = \epsilon_0$ ) and since  $|0\rangle\langle 0| + \sum_{\epsilon \neq \epsilon_0} \{\epsilon\} \langle \epsilon|$  is the unit operator, we get

$$\begin{aligned} \mathcal{U} &= V - E_0(\vec{R}) + \sum_{\epsilon > \epsilon_0} \epsilon (|\epsilon\rangle \langle \epsilon| - \{\epsilon\} \langle \epsilon\}) \\ &\quad + \epsilon_0 |\epsilon_0\rangle \langle \epsilon_0| + \epsilon_0 \sum_{\epsilon > \epsilon_0} \{\epsilon\} \langle \epsilon\} \\ &= V - [E_0(\vec{R}) - \epsilon_0] + \sum_{\text{all } \epsilon} (\epsilon - \epsilon_0) (|\epsilon\rangle \langle \epsilon| - \{\epsilon\} \langle \epsilon\}), \end{aligned} \quad (5)$$

since  $|\epsilon_0\rangle \langle \epsilon_0| = 1 - \sum_{\epsilon > \epsilon_0} |\epsilon\rangle \langle \epsilon|$ . Should there be further quantum numbers  $\alpha$ , besides  $\epsilon$ , the sum extends over these too, the states  $|\epsilon\rangle$ , etc., being then denoted by  $|\epsilon, \alpha\rangle$ , etc.

The form (5) has a certain resemblance to the pseudopotential encountered in band-structure calculations. Evidently, because of the very last term of (5),  $\mathcal{U}$  is nondiagonal in the configuration space  $\vec{r}$  of the electron variables but remains local in  $\vec{R}$  space.

If the reaction and desorption processes are slow, it is sufficient to use a Fermi's "golden-rule" calculation of the rate coefficients. Neglecting nonadiabatic effects altogether, the eigenfunctions of the total Hamiltonian ( $\mathcal{U}$  + the nuclear kinetic energy) are

$$\chi_n(\vec{R}) \psi(\vec{R}, \vec{r}, \epsilon, \alpha), \quad (6)$$

where  $\psi(\vec{R}, \vec{r}, \epsilon, \alpha)$  is some one of the wave functions ( $\vec{r}|0$ ),  $\langle \vec{r}|\epsilon, \alpha$ , and  $\chi_n(\vec{R})$  are the nuclear wave functions in the well  $E_0(\vec{R})$ . The probability of making a transition from the  $n$ th to the  $(n+1)$ th level of the well is then in Fermi's golden-rule approximation:

$$\begin{aligned} \omega_{n \rightarrow n+1} = & \sum_{\substack{\alpha, \epsilon \\ \alpha', \epsilon'}} \int \chi_{n+1}^*(R) \psi^*(\vec{R}, \vec{r}, \epsilon', \alpha') \langle \vec{r} | \mathcal{U} | \vec{r}' \rangle \\ & \times \chi_n(R) \psi(\vec{R}, \vec{r}', \epsilon, \alpha) \\ & \times \delta(E_{n+1}^N - E_n^N + \epsilon' - \epsilon) e^{-\beta(E_n^N + \epsilon - \epsilon_0)} \\ & \times d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}'_1 d\vec{r}'_2 \cdots d\vec{R}_1 d\vec{R}_2 \cdots, \quad (7) \end{aligned}$$

where  $E_n^{(N)}$  is the energy of the nuclear level  $n$  in the well  $E_0(\vec{R})$ .

Practical evaluation of the pseudopotential  $\mathcal{U}$  must, of course, draw on some form of approximate theory; however, the portion of  $V$  responsible for the quasistationary-level scheme will no longer be included in the evaluation of the transition probabilities.

#### IV. RAPIDITY OF CONVERGENCE

The utility of the above scheme hinges on the question of whether very few terms in the sum for  $\mathcal{U}$  suffice. For definiteness, consider the case of desorption of a hydrogen atom. When in the ground state of the well, its electron is essentially shared with the metal. It is then reasonable, as above, to consider the states  $|\epsilon\rangle$  to be the  $n_M + 1$  electron states of the metal, where  $n_M$  is the number of electrons of the pure metal. In the highly excited states of the well, however, the electron has almost entirely transferred to the hydrogen, preparatory to departure of the whole hydrogen atom. The above procedure then remains formally correct [provided terms such as  $|1\rangle E_1(\vec{R}) (|1\rangle +$  further suitably orthogonalized projectors are added to  $\mathcal{K}$ ] but becomes inconvenient. A "natural" form of the wave function analogous to (6) would then be

$$A \chi(\vec{R}, \vec{r}_1) \phi(\vec{R}, \vec{r}_2 \cdots), \quad (8)$$

where  $\phi$  is only an  $n_M$ -electron wave function and  $A$  the antisymmetrizer for the electron coordinates. The problem is that at sufficiently large values of  $R$  (correspondingly to a highly excited but still bound state of the  $H$  atom),  $E_0(\vec{R})$  becomes doubly degenerate or very nearly degenerate (owing to the two spin orientations of the electron of the nearly neutral  $H$  atom). For such states a simple procedure is to no longer mention the electron on the hydrogen atom, except insofar as it leads to the spin degeneracy. In place of  $|0\rangle$ , one now has  $|0, m\rangle$ ,  $m = \pm \frac{1}{2}$ , and in place of the  $\{\epsilon\}$ , one considers the states  $\{\epsilon, m\}$  obtained by orthogonalizing the states

$$|\epsilon, m\rangle - |0, m\rangle \langle 0, m | \epsilon, m \rangle. \quad (9)$$

Here  $|\epsilon, m\rangle$  is the direct product state  $|\epsilon\rangle \times |m\rangle$ , but now  $|\epsilon\rangle$  is one of the  $n_M$ -electron states of the metal. The approximate form of the potential well is shown in Fig. 1.

There is a crossover point  $R_{\text{crit}}$ , which, in the sense of the Hartree-Fock approximation separates the nondegenerate (i. e., nonmagnetic) from the degenerate (or "magnetic") regime. Actually, for  $R > R_{\text{crit}}$  the very lowest states may still be nondegenerate in the sense of Kondo compensation,<sup>5</sup> but the states whose energies exceed that of the lowest ones by the Kondo condensation energy will be degenerate. In this sense, one might say that as  $R$  increases through  $R_{\text{crit}}$ , the Kondo condensation energy decreases from a large to a small value.

As for the pseudopotential  $\mathcal{U}$ , it evidently acquires a spin-dependent part for  $R > R_{\text{crit}}$ . We may pursue the same analysis that led to expression (5), but we now base it on state vectors such as (9). We note that both  $\langle \pm \frac{1}{2} | 0, \frac{1}{2} \rangle$  are nonvanishing. Consequently, the contribution to  $\mathcal{U}$  which equals  $-\sum (\epsilon - \epsilon_0) \{\epsilon\} \langle \epsilon \rangle$  is a nondiagonal matrix in the spin space of the electron on the hydrogen atom.

In general, both the spin-independent and the spin-dependent parts of  $\mathcal{U}$  will not only be nonlocal but will also be a many-particle potential. In special cases, such as the Newns-Anderson model,<sup>6</sup> it can be approximated by a single-particle poten-

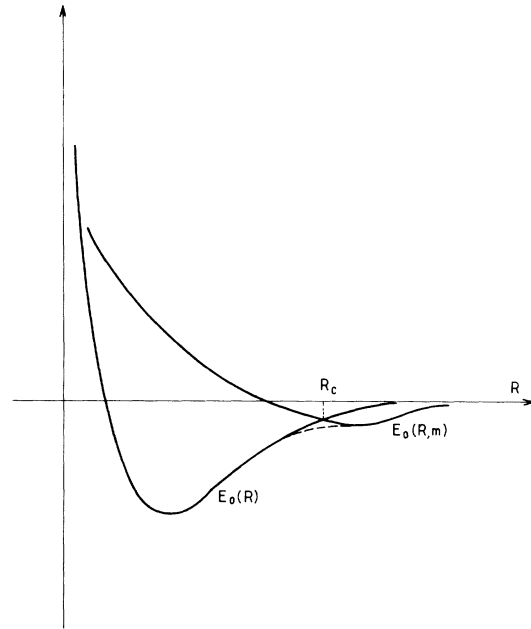
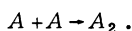


FIG. 1. Approximate form of potential well for ionized and neutral hydrogen. For  $R > R_c$ , the ground state acquires twofold degeneracy.

tial. For  $R > R_{\text{crit}}$ , the spin-dependent part then takes the form of an " $\vec{S} \cdot \vec{S}$ " interaction.<sup>7</sup> These and related matters will be discussed in a forthcoming paper.

### V. DISCUSSION

To further clarify the role of the pseudopotential in a surface reaction, we consider a purely schematic model of such a reaction. Suppose that two atoms  $A$ , adsorbed on a substrate, are capable of unrestricted motion parallel to the surface and furthermore that the same atoms in free space have a vanishingly small cross section for the reaction



(The cross section can be inhibited due to an inadequate mechanism for disposing of the binding energy of  $A_2$ .)

Consider two atoms  $A$  at equal distance  $Z$  from the surface. The energy contours, as shown in Fig. 2, can be divided in three regions. Region I ( $Z$  large and the relative distance  $r_T$  small) corresponds to free  $A_2$ . Region II ( $Z$  of order  $Z_{A_2}$ , the distance of the isolated minimum in the energy surface, and  $r_T$  still small) corresponds to adsorbed  $A_2$ . Region III ( $Z$  small and  $r_T$  large) corresponds to two dissociatively adsorbed  $A$  atoms. Region IV corresponds to free  $2A$ .

Consider now a head-on collision of the two  $A$  atoms, moving parallel to the surface and confined to the free-atom region IV. (This confinement only negligibly affects the possibility of their moving exactly parallel to the surface). In region I, there will be a semicontinuous spectrum (continuous with respect to motion normal to  $Z$  and discrete otherwise), and in region II there will be a few discrete levels. If  $\mathcal{U}$  were zero, the incident wave representing the two free atoms would re-emerge from regions I and II with unchanged total flux (though some scattering will have occurred). Stated otherwise, the occupation numbers of the various states (continuum or otherwise) will be constants of the motion. There is also some mild quasistationary character engendered by the existence of several minima, with separately derived approximate level schemes. Tunneling between these destroys the stationary nature of the levels, but in general, this effect will be small compared

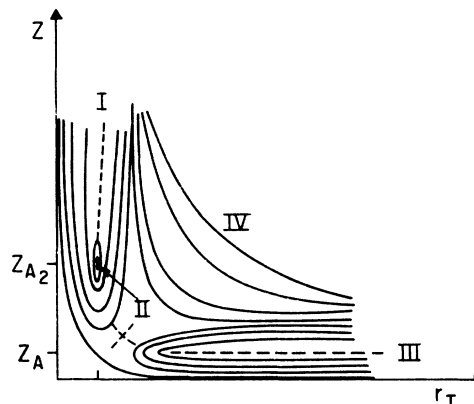


FIG. 2. Energy contours in  $Z - r_T$  plane for two atoms.

with that due to  $\mathcal{U}$ . Then the reaction  $2A \rightarrow A_2$  cannot occur. On the other hand, if  $\mathcal{U}$  is finite the initially empty levels of regions I and II will gradually become populated, according to the master equation (or its generalization to continuous indices). In this way the reaction  $2A \rightarrow A_2$  does take place,  $\mathcal{U}$  acting as a means of damping.

It is evident that one can dispense with a quantum-mechanical description of the atomic motions of the adatoms altogether, given the energy surface  $E(R)$ . The master equation turns into the Boltzmann equation, with  $dn/dt$  becoming the total time derivative (including the change due to the "systematic" part of the effective potential energy). The transition terms calculated using  $\mathcal{U}$  turn into the collision terms.

A detailed derivation of such a description (including application to the inverse case of  $A_2$  dissociation on the surface) will be given in a later paper.

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PHYSICAL REVIEW B

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## Electromagnetic Generation of Ultrasonic Waves in Bismuth<sup>†</sup>

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Measurements were made of electromagnetic generation of ultrasonic shear and longitudinal waves at liquid-helium temperatures in several single crystals of bismuth for each of the three principal crystallographic axes. Measurements were made over the frequency range 5–50 MHz. In addition to giant quantum oscillations (GQO) in the generation efficiency, which were observed in all cases, detailed studies of a pronounced low-field (30–300 G) peak in the generation efficiency are reported. This peak is seen both for shear- and longitudinal-wave generation and is found to depend strongly on a number of parameters, including temperature, rf field strength, frequency, and crystallographic orientation. The frequency dependence of the shear-wave measurements is compared with the recent helicon-phonon interaction theory of Quinn.

### I. INTRODUCTION

The generation of sound waves directly from electromagnetic radiation incident upon a metal surface in the presence of a static magnetic field was first discovered by Larson and Saermark.<sup>1</sup> The classical explanation for this effect derives essentially from the Lorentz force on the eddy currents induced in the rf skin depth of the metal and is consistent with the dependence of the observed sound polarization on geometry as well as the strictly linear field dependence up to 140 kG. A number of experiments<sup>2</sup> have been carried out on a variety of metals, both in the classical limit and at liquid-helium temperatures. A reasonably general theory of electromagnetic sound generation in a free-electron metal has been given by Quinn.<sup>3</sup> The results of this calculation are in good agreement with measurements on potassium at helium temperatures by Turner *et al.*<sup>2</sup>

All of the early experiments on electromagnetic sound generation in metals were performed in situations where quantum effects were comparatively unimportant. Following the intuitive notion that the same electron-phonon interaction responsible for the attenuation of a propagating wave is also fundamentally the source of the sound generation at the metal surface, Dobbs *et al.*<sup>4</sup> observed giant quantum oscillations (GQO) in the generation of shear waves in Bi at liquid-helium temperatures. Since then, GQO have also been reported in the

generation of longitudinal sound waves in Bi.<sup>5</sup> Further observations of these quantum effects in Bi are summarized in this paper.

In addition to the Landau-level effects in Bi which had been anticipated in the generation efficiency from simple reciprocity arguments, a very unusual large peak was also observed in the generation of shear waves along a binary axis at low fields. A similar peak was later observed in the longitudinal-wave configuration.<sup>5</sup> These effects have also been reported independently by Gantmakher and Dolgoplov,<sup>6</sup> using cw techniques and have no apparent counterpart in the attenuation, which varies monotonically in the field region 30–300 G for which the low-field peak in the generation occurs. A detailed experimental study of this low-field peak for all possible sound modes along the binary, bisectrix, and trigonal axes is presented in this paper.

### II. EXPERIMENTAL TECHNIQUE

#### A. Samples

In this study six primary samples from different sources were used (see Table I). Four samples are oriented single crystals, the other two polycrystalline with large-size grains. The nominal starting purity ranged from reagent grade to zone refined (99.99995% pure); the thicknesses of the samples were from 2–20 mm. Orientations were found to be within 2° of a binary, bisectrix, or trigonal axis (hereafter referred to as X, Y, or Z, respectively).

Just prior to making measurements, the sample