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A one-electron perturbation theory of chemisorption

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We present a general one-electron perturbation theoretic formalism for the interaction of discrete molecules or a translationally periodic array of molecules with a surface. The approach uses a Green's function formalism, a perturbation expansion and a technique of calculating the imaginary parts of traces over matrix products. The methodology, applicable to both Hückel and extended Hückel calculations, introduces projected Green's functions which serve as natural indices for the reactivity, inherent and mutual, of different surface sites.

Molecules reacting, a molecule interacting with a surface—these are systems quite naturally made up of two or more pieces or subsystems. We know their orbitals when they are separate, perhaps approximately. And we want to know their orbitals as they interact, the energetics and orientation of their reaction.

The natural language for the analysis of chemical reaction, the interaction of two chemical subsystems, is perturbation theory. The zeroth-order wave functions, presumably, if imperfectly, known, are those of the separate or isolated molecules. The perturbation is their interaction, weak or strong.

Chemisorption should be analyzed, in principle, in a many-electron framework. In practice, a one-electron perturbation theory approach is often adequate, qualitatively or semiquantitatively. More than that, a one-electron perturbation theoretic approach lends itself to an analysis of trends as a function of atom or ligand electronegativity, donor or acceptor character, etc., i.e., nothing more or less than a *chemical* analysis. Witness the remarkable success of frontier orbital theory[1,2] which is just the implementation of a simplified one-electron perturbation theoretic approach[3,4] to chemical reactivity.

In recent times one of us (RH) has worked extensively on extended systems; one-, two-, and three-dimensional materials. One of the foci of interest has been the chemisorption and reaction of molecules on surfaces. In the course of this work[5] it became apparent that a qualitative perturbation approach to extended systems was very much needed.

What we present here then is a systematic perturbational treatment of extended chemical systems, considered as consisting of a pair of interacting subsystems. The sporadic, though fruitful, attempts to use this approach in the recent literature[6,7] operate with the second-order energy correction known from molecular quantum chemistry. Such an extrapolation is obvious for one-dimensional structures.[8] For the extended systems of higher dimensionality, due to the degeneracy of energy levels, the situation is less clear. The problem is important, and it certainly merits a careful derivation. The formulas for the interaction energy in an extended system we obtain here, although having a familiar physical (or chemical) interpretation, possess an advantage of being directly related to widely available band structure calculations. Some novel qualitative concepts also arise in our treatment, such as new surface reactivity indices for chemisorption and a new phenomenological approach based on the modeling of the energy dependence of the density of states (DOS).

The application of these concepts in a qualitative theory of chemisorption heats seems promising. For instance, the main problem here is an adequate account of the energy dependence of an interaction matrix element between an adsorbate molecule and a surface. The reported attempts to overcome this difficulty[6,7] neglect the specific features of a real surface band structure. This problem is, however, solved in our treatment. The application to specific chemical problems will follow in future papers.

I. THE GENERAL DOS EXPANSION

We consider the Hamiltonian

$$H = H_0 + V, \tag{1.1}$$

where H_0 is a zero-order Hamiltonian and V is a perturbation. We assume that H_0 always possesses translational symmetry. For V two cases will be considered: (a) translationally symmetrical perturbation; (b) local perturbation. So we have the Schrödinger equations

$$(H - E_i)\Psi_i(r) = 0,$$
$$(H_0 - \epsilon_i)\varphi_i(r) = 0, \tag{1.2}$$

and the corresponding Green's operators

$$G(E) = \frac{1}{E + i\delta - H}$$
$$\qquad\qquad (\delta \to +0). \tag{1.3}$$
$$G_0(E) = \frac{1}{E + i\delta - H_0}$$

The coordinate representation of $G_0(E)$ (i.e., the Green's function) is

$$G_0(r, r'|E) = \sum_i \frac{\varphi_i^*(r)\varphi_i(r')}{E + i\delta - \epsilon_i}. \tag{1.4}$$

The zero-order eigenfunctions $\varphi_i(r)$ are Bloch Molecular Orbitals (MOs). Finally, the usual definition of the DOS[9] will be made

$$n(E) = \sum_i \delta(E - E_i),$$

$$n_0(E) = \sum_i \delta(E - \epsilon_i). \tag{1.5}$$

The perturbation expansion for $n(E)$ can be derived from the following basic relation:

$$n(E) - n_0(E) = -\frac{1}{\pi}\frac{\partial}{\partial E}\, \text{Im}\left\{\ln \frac{\det(E + i\delta - H)}{\det(E + i\delta - H_0)}\right\}. \tag{1.6}$$

This formula has been obtained[10,11] starting from the definition (1.3) of the Green's function, and using the identity

$$\lim_{\delta \to 0}\frac{1}{x + i\delta - x'} = P\left(\frac{1}{x - x'}\right) - i\pi\delta(x - x'), \tag{1.7}$$

where P stands for the principal part operator. Relation (1.6) obviously reduces to

$$n(E) - n_0(E) = -\frac{1}{\pi}\frac{\partial}{\partial E}\, \text{Im}\{\ln \det[1 - G_0(E)V]\}. \tag{1.8}$$

This closed form has been used by Einstein and Schrieffer.[10] We extend their treatment by applying the identity[12]

$$\det(1 + A) = \exp\left\{\sum_{m=1}^{\infty}\frac{(-1)^{m-1}}{m}\, \text{tr}\, A^m\right\} \tag{1.9}$$

which results in the following perturbation series:

$$n(E) - n_0(E) = \frac{1}{\pi}\frac{\partial}{\partial E}\, \text{Im}\sum_{m=1}^{\infty}\frac{1}{m}\, \text{tr}[G_0(E)V]^m. \tag{1.10}$$

This formula will serve us as a basis for our subsequent considerations.

II. THE ENERGY AND QUASIMOMENTUM REPRESENTATIONS

We need matrix representation of operators $G_0(E)$ and V for the trace calculations in Eq. (1.10). Different MO representations are available, due to the degeneracy of levels ϵ_i. We shall deal with two of them:

$$\varphi_i \to |Er\rangle \tag{2.1}$$

(E representation),

$$\varphi_i \to |k\alpha\rangle \tag{2.2}$$

(k representation).

In Eq. (2.1) the energy E is taken as a main quantum number, the second number r labeling the states having the same energy E; $r = r(E)$. Another, more customary representation (2.2), takes the reciprocal lattice vector k (the quasimomentum) as the main quantum number, α being a band index. Either representation (2.1) or (2.2) will be convenient, depending on the particular applications.

The quantities E and k are considered as continuum variables, and that is why one should also define the prescriptions for transforming a sum Σ_i into integrals over E or k. This depends on the normalization accepted for continuum basis functions. In the E representation it is convenient to work with the scattering theory prescription:[13]

$$\langle Er|E'r'\rangle = \delta_{rr'}\delta(E - E'). \tag{2.3}$$

Then

$$\sum_i \to \int dE \sum_{r(E)}. \tag{2.4}$$

The conventional basis functions for k representation are Bloch MOs normalized to unity:

$$\langle k\alpha|k\beta\rangle = \delta_{\alpha\beta}$$

$$\langle k\alpha|k'\beta\rangle = 0 \quad (k' \neq k). \tag{2.5}$$

Then, denoting the total volume as Ω, we obtain a standard relation[14]

$$\frac{1}{\Omega}\sum_i \to \int \frac{dk}{(2\pi)^p}\sum_\alpha, \tag{2.6}$$

where $p = 2$ or 3 for the surface and bulk cases, respectively.

Let $\epsilon_\alpha(k)$ be the zeroth approximation band energy function. We denote by $k = k_\alpha(E)$ the multivalued quantity satisfying the equation $\epsilon_\alpha(k) = E$. Then the following identity is valid:

$$\Omega \int \frac{dk}{(2\pi)^p}\sum_\alpha \delta[k - k_\alpha(E)] = n_0(E). \tag{2.7}$$

Finally, the interrelation between E and k representations is given by

$$\sum_{r(E)}\langle Er| = \Omega \int \frac{dk}{(2\pi)^p}\sum_\alpha \delta[k - k_\alpha(E)]\langle k\alpha|. \tag{2.8}$$

III. ENERGY REPRESENTATION

Formula (1.10) supplies us with the expansion of the DOS in terms of powers of V:

$$n(E) - n_0(E) = n^{(1)}(E) + n^{(2)}(E) + \dots . \tag{3.1}$$

Let us consider the two leading terms of this expansion.

First order:

$$n^{(1)}(E) = \frac{1}{\pi}\frac{\partial}{\partial E}\, \text{Im}\int dE'\sum_{r(E')}\frac{\langle E'r|V|E'r\rangle}{E + i\delta - E'}.$$

The Im operation is performed according to Eq. (1.7). So we obtain

$$n^{(1)}(E) = -\frac{\partial}{\partial E}\sum_{r(E)}\langle Er|V|Er\rangle. \tag{3.2}$$

Second order: The evaluation of the corresponding term of Eq. (1.10) again using (1.7) for the Im calculation, gives

$$n^{(2)}(E) = -\frac{\partial}{\partial E}\sum_{r(E)}\fint dE'\sum_{s(E')}\frac{|\langle Er|V|E's\rangle|^2}{E - E'} \tag{3.3}$$

where $\fint$ means the Cauchy principal value of the integral.

The case important for what follows implies vanishing of all interaction matrix elements, including diagonal ones, between degenerate Bloch functions:

$$\langle Er|V|Es\rangle = 0. \tag{3.4}$$

This simplifies the expansion terms to

$$n^{(1)}(E) = 0,$$

$$n^{(2)}(E) = -\frac{\partial}{\partial E}\left\{\sum_{r(E)}\int dE'\sum_{s(E')}\frac{|\langle Er|V|E's\rangle|^2}{E - E'}\right\}. \tag{3.5}$$

Now let us consider the case when matrix elements $(Er|V|E's)$ are r,s independent:

$$(Er|V|E's) = (E|V|E'). \tag{3.6}$$

It is then possible to change the normalization of the basis functions and pass from the δ-function normalized eigenfunctions $|Er)$ to functions $|Er\rangle$, normalized to unity according to

$$\langle Er|Es\rangle = \delta_{rs},$$

$$\langle Er|E's\rangle = 0 \quad (E' \neq E). \tag{3.7}$$

As is readily seen from the comparison with Eq (2.5), the functions $|Er\rangle$ so defined differ from functions $|k\alpha\rangle$ only by the choice of the quantum numbers labeling them.

In this case we can make formal changes in relation (2.8) according to:

$$(Er| \to (E|$$

$$\delta[k - k_\alpha(E)]\langle k\alpha| \to \delta[k - k_\alpha(E)]\langle E|.$$

Thus we obtain, by combining Eqs. (2.7) and (2.8),

$$\sum_{r(E)}\sum_{s(E')}\frac{|(Er|V|E's)|^2}{E-E'} = \frac{|\langle E|V|E'\rangle|^2}{E-E'}n_0(E)n_0(E'),$$

where $\langle E|V|E'\rangle$ stands for $\langle Er|V|E's\rangle$ according to Eq. (3.6). With this new notation (3.5) is transformed into

$$n^{(2)}(E) = -\frac{\partial}{\partial E}\left\{n_0(E)\int dE'n_0(E')\frac{|\langle E|V|E'\rangle|^2}{E-E'}\right\}. \tag{3.8}$$

It is then expedient to transform the general expression (3.3) into the form of Eq. (3.8), defining a quantity

$$R(E,E') = \frac{1}{n_0(E)n_0(E')}\sum_{r(E)}\sum_{s(E')}|(Er|V|E's)|^2. \tag{3.9}$$

This is nothing else but an averaged squared absolute value of the interaction matrix element. With this definition (3.3) converts into

$$n^{(2)}(E) = -\frac{\partial}{\partial E}\left\{n_0(E)\int dE'n_0(E')\frac{R(E,E')}{E-E'}\right\}. \tag{3.10}$$

The meaning of this transformation is that the integral in curly brackets is expected to depend on E much more smoothly than $n_0(E)$ does. That is why a reasonable approximation may be

$$n^{(2)}(E) \cong -\left\{\int dE'n_0(E')\frac{R(E,E')}{E-E'}\right\}\frac{dn_0(E)}{dE}. \tag{3.11}$$

When the matrix elements are r,s independent we obtain $R(E,E') = |\langle E|V|E'\rangle|^2$.

An example of using approximate relation (3.11) is given in the Appendix A.

IV. QUASIMOMENTUM REPRESENTATION

We start with the case when both operators H_0 and V are characterized by translational symmetry. Then the matrices of operators $G_0(E)$ and V consist of diagonal blocks, the blocks of $G_0(E)$, being diagonal by themselves:

$$\langle k\alpha|G_0(E)|k'\beta\rangle = \langle k\alpha|V|k'\beta\rangle = 0 \quad (k \neq k') \tag{4.1}$$

$$\langle k\alpha|G_0(E)|k\beta\rangle = G_{\alpha\alpha}(E,k)\delta_{\alpha\beta}, \tag{4.2}$$

$$\langle k\alpha|V|k\beta\rangle = V_{\alpha\beta}(k),$$

where

$$G_{\alpha\alpha}(E,k) = \frac{1}{E + i\delta - \epsilon_\alpha(k)}. \tag{4.3}$$

That is why the trace in Eq. (1.10) becomes a sum over traces of individual blocks. According to Eq. (2.6) we obtain

$$\frac{1}{\Omega}[n(E) - n_0(E)]$$

$$= \frac{1}{\pi}\frac{\partial}{\partial E}\mathrm{Im}\sum_{m=1}^\infty\frac{1}{m}\int\frac{dk}{(2\pi)^p}\mathrm{tr}[G_0(E,k)V(k)]^m, \tag{4.4}$$

where $G_0(E,k)$ and $V(k)$ are the block submatrices built of elements (4.2) and (4.3).

Now we can invoke the invariance of the trace operation under a unitary basis transformation, and pass on to the Bloch atomic orbital (AO) basis. We consider here a simple Hückel model with an orthogonal AO basis. Then the form of V can be explicitly displayed. This is illustrated by a special case when the zeroeth approximation is a combination of a pair of noninteracting sublattices "A" and "B". Their interaction is assumed to generate only intersublattice matrix elements, leaving unchanged intrasublattice ones. So the structure of the matrices in the Bloch AO basis will be

$$G_0(E,k) = \left(\begin{array}{c|c}G^A & 0 \\ \hline 0 & G^B\end{array}\right); V(k) = \left(\begin{array}{c|c}0 & \beta \\ \hline \beta^\dagger & 0\end{array}\right), \tag{4.5}$$

where "$\dagger$" means the Hermitian conjugate. Using the special block structure of matrices (4.5), we reduce Eq. (4.4) to the final form

$$\frac{1}{\Omega}[n(E) - n_0(E)]$$

$$= \frac{1}{\pi}\frac{\partial}{\partial E}\sum_{m=1}^\infty\frac{1}{m}\int\frac{dk}{(2\pi)^p}\mathrm{tr}[G^A\beta G^B\beta^\dagger]^m. \tag{4.6}$$

The k representation is most convenient for practical explicit calculations. The general prescription for calculating the Green's matrix $G_0(E,k)$ in the Bloch AO basis is the following: Let $H_0(k)$ be a Hamiltonian matrix, in this basis diagonalized by a unitary matrix $C(k)$:

$$C^\dagger(k)H_0(k)C(k) = \epsilon(k), \tag{4.7}$$

where $\epsilon(k)$ is a diagonal matrix of the band energies. Then

$$G_0(E,k) = C(k)[(E + i\delta)I - \epsilon(k)]^{-1}C^\dagger(k). \tag{4.8}$$

V. ENERGY CALCULATIONS

The perturbational correction to the total energy density is calculated as

$$\Delta E = \frac{1}{\Omega}(E_{\mathrm{tot}} - E_0)$$

$$= \frac{2}{\Omega}\left[\int_{-\infty}^{E_F}En(E)dE - \int_{-\infty}^{\epsilon_F}En_0(E)dE\right], \tag{5.1}$$

where E_F and ϵ_F are Fermi levels for a perturbed and an unperturbed system. The closed expression following from Eq. (5.1) was derived by Einstein and Schrieffer:[10]

$$\Delta E = -\frac{2}{\pi\Omega} \int_{-\infty}^{\epsilon_F} \text{Im} \ln \det[1 - G_0(E)V]dE. \quad (5.2)$$

We substitute Eq. (1.9) into Eq. (5.2) to obtain the general perturbation expansion

$$\Delta E = -\frac{2}{\pi\Omega} \text{Im} \sum_{m=1}^{\infty} \frac{1}{m} \int_{-\infty}^{\epsilon_F} \text{tr}[G_0(E)V]^m dE. \quad (5.3)$$

Alternatively one may obtain the same expression starting from the basic formula:[10,15]

$$\Delta E = \frac{2}{\Omega} \left\{ \int_{-\infty}^{\epsilon_F} (E - \epsilon_F)[n(E) - n_0(E)]dE \right\}. \quad (5.4)$$

Substitution of $[n(E) - n_0(E)]$ from Eq. (1.10) and integrating by parts again gives Eq. (5.3).

Now we return to a special type of perturbation matrix, as given by Eq. (4.5), for which the first-order correction vanishes, and write out the second-order energy correction.

A. Energy representation

If we use formula (3.10) in (5.4) the result is

$$\Delta E = \frac{2}{\Omega} \int_{-\infty}^{\epsilon_F} n_0(E) \int_{-\infty}^{\infty} dE' \, n_0(E')$$

$$\times \frac{R(E - E')}{E - E'} dE \, dE'. \quad (5.5)$$

We now observe that the integrand in Eq. (5.5) is antisymmetric under the permutation of E and E'. This results in vanishing of the part of Eq. (5.5) corresponding to symmetrical limits

$$\int_{-\infty}^{\epsilon_F} \int_{-\infty}^{\epsilon_F} dE \, dE' (\cdots) = 0.$$

That is why the final result is

$$\Delta E = \frac{2}{\Omega} \int_{-\infty}^{\epsilon_F} n_0(E)dE \int_{\epsilon_F}^{\infty} n_0(E')dE' \frac{R(E,E')}{E - E'}. \quad (5.6)$$

It should be noted that the same result (5.6) is valid without invoking approximation (3.5) as the second-order energy term. Indeed, in this case Eq. (5.5) becomes the second-order correction provided the second integral is substituted by its principal part

$$\left(\int_{-\infty}^{\infty} \to \fint \right).$$

The following reasoning again gives Eq. (5.6).

B. Quasimomentum representation

If we use Eq. (4.4) in Eq. (5.4), then integration by parts yields

$$\Delta E = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{\epsilon_F} dE \int \frac{dk}{(2\pi)^p} \text{tr}[G_0(E,k)V(k)]^2. \quad (5.7)$$

Let us calculate the trace using the Bloch MO basis:

$$\text{tr}[G_0(E,k)V(k)]^2 = \sum_{\alpha\beta} \frac{1}{E + i\delta - \epsilon_\alpha(k)} |\langle k\alpha|V|k\beta\rangle|^2$$

$$\times \frac{1}{E + i\delta - \epsilon_\beta(k)}.$$

So only Green's functions should be considered as complex quantities when calculating "Im." This is a general result, valid for any perturbational order m in the case V is Hermitian (see also Appendix B). After using Eq. (1.7) we obtain

$$\text{Im tr}[G_0(E,k)V(k)]^2 = -2\pi \sum_{\alpha,\beta} \delta[E - \epsilon_\alpha(k)]$$

$$\times P \frac{|\langle k\alpha|V|k\beta\rangle|^2}{\epsilon_\alpha(k) - \epsilon_\beta(k)}.$$

Integration of Eq. (5.7) now gives

$$\Delta E = 2 \sum_{\alpha\beta} \int \frac{dk}{(2\pi)^p} \vartheta[\epsilon_F - \epsilon_\alpha(k)] \frac{|\langle k\alpha|V|k\beta\rangle|^2}{\epsilon_\alpha(k) - \epsilon_\beta(k)}, \quad (5.8)$$

where ϑ is the Heaviside step function.

At this stage we consider a situation when one of sublattices is formed by noninteracting subsystems having a discrete spectrum. This corresponds roughly to the case of adsorption on a surface at low coverage. The sums are subdivided as

$$\sum_{\alpha(\beta)} \to \sum_{i(j)} + \sum_{\alpha(\beta)},$$

where i,j correspond to discrete k-independent levels with energies ϵ_i, ϵ_j, whereas α,β now count only true bands of the substrate surface. Since we have assumed that $\langle i|V|j\rangle = \langle\alpha k|V|\beta k\rangle = 0$, Eq. (5.8) reduces to

$$\Delta E = 2\left\{ \sum_{i(\epsilon_i < \epsilon_F)} \sum_\alpha \int \frac{dk}{(2\pi)^2} \frac{|\langle i|V|k\alpha\rangle|^2}{\epsilon_i - \epsilon_\alpha(k)} \vartheta[\epsilon_\alpha(k) - \epsilon_F] \right.$$

$$- \sum_{i(\epsilon_i > \epsilon_F)} \sum_\alpha \int \frac{dk}{(2\pi)^2} \frac{|\langle i|V|k\alpha\rangle|^2}{\epsilon_i - \epsilon_\alpha(k)}$$

$$\left. \times \vartheta[\epsilon_F - \epsilon_\alpha(k)] \right\}. \quad (5.9)$$

Formula (5.9) has a simple interpretation as

$$\tfrac{1}{2}\Delta E = \begin{cases} \text{sum of shifts of occupied discrete levels} \\ \text{due to their interaction with an unoccupied} \\ \text{part of the band spectrum} \end{cases}$$

$$- \begin{cases} \text{sum of shifts of unoccupied discrete levels} \\ \text{due to their interaction with an occupied} \\ \text{part of the band spectrum} \end{cases}.$$

This result is often used in qualitative theories of adsorption, being derived as an intuitive extrapolation of the expression for the second-order interaction energy, well known from molecular quantum chemistry. It is derived here directly from band theory. It could be also obtained in the energy representation if the DOS's $n_0(E)$ and $n_0(E')$ in Eq. (5.6) were subdivided into discrete and continuum parts.

VI. THE MODEL OF ADSORPTION WITHOUT IMPOSED SYMMETRY

For the case of a single molecule adsorbed on a surface we start from Eq. (5.3), considering $G_0(E)$ as a Green's operator for a combined system built of the noninteracting molecule and the surface. Operator V denotes a localized interaction. We use now an AO basis (but not a Bloch AO basis!) for the representation of operators G_0 and V. The block structure of the corresponding matrices is

$$G_0(E) = \begin{pmatrix} G^M & 0 \\ 0 & G^\Sigma \end{pmatrix}; \quad V = \begin{pmatrix} 0 & v \\ v^\dagger & 0 \end{pmatrix}. \tag{6.1}$$

Here G^M and G^Σ are the Green's matrices of isolated molecule and surface (in the AO basis) and v is an interaction matrix, which is real in the present case.

The second order of formula (5.3) gives

$$\Delta E = -\frac{1}{\pi\Omega} \mathrm{Im} \int_{-\infty}^{\epsilon_F} \mathrm{tr}[G_0(E)V]^2 dE$$

$$= -\frac{2}{\pi\Omega} \mathrm{Im} \int_{-\infty}^{\epsilon_F} \mathrm{tr}[G^M v G^\Sigma v^\dagger]\, dE. \tag{6.2}$$

The calculation (evaluation of "Im") proceeds from this point in the manner described in Sec. V.

The following notations are used below:

(a) $|\chi_r\rangle$, $|\chi_s\rangle$—AOs of the adsorbate molecule; $|\chi_\mu(R)\rangle$, $|\chi_\nu(R')\rangle$—AOs of the surface.

(b) i—the indices labeling MOs of the molecule:

$$|i\rangle = \sum_r |\chi_r\rangle C_{ri};$$

ϵ_i being the corresponding energy levels.

(c) The Bloch MOs of an isolated surface are

$$|k\alpha\rangle = \frac{1}{\sqrt{N}} \sum_{\nu,R} |\chi_\nu(R)\rangle e^{ikr} C_{\nu\alpha}(k), \tag{6.3}$$

where N is the number of unit cells in the surface.

(d) $V_{r\nu} = v_{r\nu} = v_{\nu r}^\dagger = V_{\nu r}$—the real interaction matrix elements of matrices v and $v^\dagger$:

$$v_{r\nu}(R) = \langle \chi_r|V|\chi_\nu(R)\rangle = V_{r\nu}(R),$$

$$v_{\nu r}^\dagger(R) = \langle \chi_\nu(R)|V|\chi_r\rangle = V_{\nu r}(R). \tag{6.4}$$

(e) $G_{\mu\nu}^-(E,R-R')$

$$= \sum_\alpha \int \frac{dk}{(2\pi)^2} \frac{1}{2} [C_{\mu\alpha}(k)C_{\nu\alpha}^*(k)e^{ik(R-R')}$$

$$+ C_{\nu\alpha}(k)C_{\mu\alpha}^*(k)e^{ik(R'-R)}]$$

$$\times \frac{\vartheta[\epsilon_F - \epsilon_\alpha(k)]}{E - \epsilon_\alpha(k)}, \quad E > \epsilon_F; \tag{6.5}$$

$G_{\mu\nu}^+(E,R-R')$

$$= \sum_\alpha \int \frac{dk}{(2\pi)^2} \frac{1}{2} [C_{\mu\alpha}(k)C_{\nu\alpha}^*(k)e^{ik(R-R')}$$

$$+ C_{\nu\alpha}(k)C_{\mu\alpha}^*(k)e^{ik(R'-R)}]$$

$$\times \frac{\vartheta[\epsilon_\alpha(k) - \epsilon_F]}{E - \epsilon_\alpha(k)}; \quad E < \epsilon_F.$$

The resulting expression, calculated starting from Eq. (6.2), is

$$\Delta E = \frac{2}{N} \left\{ \sum_{\substack{i \\ (\epsilon_i < \epsilon_F)}} \sum_{rs} \sum_{\substack{\mu R \\ \nu R'}} C_{ri} C_{si} V_{r\mu}(R) V_{s\nu}(R') \right.$$

$$\times G_{\mu\nu}^+(\epsilon_i, R-R') - \sum_{\substack{i \\ (\epsilon_i > \epsilon_F)}} \sum_{rs} \sum_{\substack{\mu R \\ \nu R'}} C_{ri} C_{si} V_{r\mu}(R)$$

$$\left. \times V_{s\nu}(R') G_{\mu\nu}^-(\epsilon_i, R-R') \right\}. \tag{6.6}$$

It is easy to show that expressions (5.9) and (6.6) are the same, with the only difference being the factor N^{-1}. This appears because we dealt with a single molecule in this section, whereas N molecules were adsorbed according to the derivation of Sec. V. This means that in the second order of perturbation there is no through-surface interaction between adsorbate molecules. This interaction appears only in the next expansion term of Eq. (5.3), which corresponds to the fourth order of perturbation ($\sim V^4$).

According to Eq. (6.5) the quantity $G_{\mu\mu}^+(E,0)$ is a measure of the affinity of surface site μR towards a donor level (doubly occupied) with energy $E < \epsilon_F$. The quantity $[-G_{\mu\mu}(E,0)]$ measures the same towards an acceptor level (unoccupied) with $E > \epsilon_F$. Both quantities are always negative, as follows from their definition (6.5). The off-diagonal quantities $G_{\mu\nu}^\pm(E,R-R')$ measure a combined reactivity of a pair of sites μR, $\nu R'$. We shall call these quantities "projected Green's functions" because they perform the projection of a regular surface Green's function onto subspaces of occupied (G^-) and unoccupied (G^+) surface MOs.

VII. RELATION BETWEEN LOCAL DOS'S AND PROJECTED GREEN'S FUNCTIONS

We define the local DOS matrix of a surface $\eta_{\mu\nu}(E,R-R')$ by the relation

$$\eta_{\mu\nu}(E,R-R')$$

$$= \frac{1}{\Omega} n_{\mu\nu}(E,R-R')$$

$$= \sum_\alpha \int \frac{dk}{(2\pi)^2} \frac{1}{2} [C_{\alpha\mu}(k)C_{\alpha\nu}^*(k)e^{ik(R-R')}$$

$$+ C_{\alpha\nu}(k)C_{\alpha\mu}^*(k)e^{ik(R'-R)}] \delta(E - \epsilon_\alpha(k)). \tag{7.1}$$

Then we consider the surface Green's operator [see Eq. (6.1)] $G^\Sigma(E) = (E + i\delta - H^\Sigma)^{-1}$, where H^Σ is the surface Hamiltonian, and define its matrix elements as in (6.5) but without the projecting ϑ functions. According to Eq. (1.7) the imaginary parts of these matrix elements are the quantities (7.1) times $(-\pi)$. We can additionally utilize the Kramers–Kronig relations [13], stating that

$$\mathrm{Re}\, G_{\mu\nu}^\Sigma(E,R-R')$$

$$= -\frac{1}{\pi} \int_{-\infty}^{\infty} dE' \frac{\mathrm{Im}\, G_{\mu\nu}^\Sigma(E',R-R')}{E'-E}.$$

Therefore,

$$\mathrm{Re}\, G_{\mu\nu}(E,R-R') = \int_{-\infty}^{\infty} dE' \frac{\eta_{\mu\nu}(E',R-R')}{E'-E}. \tag{7.2}$$

Now we define the projected local DOS matrices by

$$\eta_{\mu\nu}^{-}(E,R-R')$$

$$= \sum_\alpha \int \frac{dk}{(2\pi)^2} \frac{1}{2} \left[C_{\alpha\mu}(k) C_{\alpha\nu}^*(k) e^{ik(R-R')} \right.$$

$$\left. + C_{\alpha\nu}(k) C_{\alpha\mu}^*(k) e^{ik(R'-R)} \right]$$

$$\times \delta[E - \epsilon_\alpha(k)] \vartheta \left[\epsilon_F - \epsilon_\alpha(k) \right], \tag{7.3}$$

$$\eta_{\mu\nu}^{+}(E,R-R') = \sum_\alpha \int \frac{dk}{(2\pi)^2} \frac{1}{2}$$

$$\times \left[C_{\alpha\mu}(k) C_{\alpha\nu}^*(k) e^{ik(R-R')} \right.$$

$$\left. + C_{\alpha\nu}(k) C_{\alpha\mu}^*(k) e^{ik(R'-R)} \right]$$

$$\times \delta[E - \epsilon_\alpha(k)] \vartheta \left[\epsilon_\alpha(k) - \epsilon_F \right].$$

The same reasoning as that leading to Eq. (7.2) relates them to real parts of the projected Green's functions (6.5):

$$\mathrm{Re}\, G_{\mu\nu}^{\pm}(E,R-R') = \int_{-\infty}^{\infty} dE' \frac{\eta_{\mu\nu}^{\pm}(E',R-R')}{E'-E}. \tag{7.4}$$

Moreover, since G^- is real for $E > \epsilon_F$ and so is G^+ for $E < \epsilon_F$, and since these are the only energy intervals we need, according to Eq. (6.5), we can write $G_{\mu\nu}^{\pm}$ instead of $\mathrm{Re}\, G_{\mu\nu}^{\pm}$ on the left-hand side of Eq. (7.4). Finally, it is obvious that

$$\eta_{\mu\nu}^{-}(E,R-R') = \eta_{\mu\nu}(E,R-R')\vartheta(\epsilon_F - E),$$

$$\eta_{\mu\nu}^{+}(E,R-R') = \eta_{\mu\nu}(E,R-R')\vartheta(E - \epsilon_F).$$

This results in the expressions

$$G_{\mu\nu}^{-}(E,R-R')$$

$$= \int_{-\infty}^{\epsilon_F} dE' \frac{\eta_{\mu\nu}(E',R-R')}{E'-E} \quad (E > \epsilon_F),$$

$$G_{\mu\nu}^{+}(E,R-R') = \int_{\epsilon_F}^{\infty} dE' \frac{\eta_{\mu\nu}(E',R-R')}{E'-E} \quad (E < \epsilon_F). \tag{7.5}$$

Thereby, given the local DOS's (7.1), we can calculate projected Green's functions by a simple integration.

VIII. THE EXTENDED HÜCKEL (EH) TREATMENT OF ADSORPTION WITHOUT IMPOSED SYMMETRY

In the EHT case we deal with secular equation:

$$H_0 C = S_0 C\epsilon; \quad C^\dagger S_0 C = I, \tag{8.1}$$

where matrices H_0, S_0, C, and ϵ correspond to the AO representations of the zero-order Hamiltonian and overlap, and to MO coefficients and energy levels. The total overlap matrix, denoted as S, has the following block structure (see Sec. VI):

$$S = S_0 + S. \tag{8.2}$$

$$S_0 = \left(\begin{array}{c|c} S^M & O \\ \hline O & S^\Sigma \end{array} \right); \qquad s = \left(\begin{array}{c|c} O & \text{⧄} \\ \hline \text{⧄} & O \end{array} \right)$$

The second-order energy expansion is derived in Appendix B. We discuss here its main features.

The Green matrix $G_0(E)$ has the diagional block structure

$$G_0(E) = \left(\begin{array}{c|c} G^M & 0 \\ \hline 0 & G^\Sigma \end{array} \right) \tag{8.3}$$

and can be expressed in the form of Eq. (4.8) as

$$G_0(E) = C(E + i\delta - \epsilon)^{-1} C^\dagger. \tag{8.4}$$

The inclusion of overlap results in a renormalization of interaction matrix V according to

$$W = S_0^{-1} V S_0^{-1}. \tag{8.5}$$

The interaction energy consists of two contributions:

$$\Delta E = \Delta E^{(1)} + \Delta E^{(2)},$$

$$\Delta E^{(1)} = -\frac{2}{\Omega} \left\{ \sum_{i(\epsilon_i < \epsilon_F)} \sum_{rs} C_{ri} C_{si} A_{rs}^M \right.$$

$$+ \frac{1}{N} \sum_\alpha \int \frac{dk}{(2\pi)^2} \vartheta \left[\epsilon_F - \epsilon_\alpha(k) \right]$$

$$\left. \times \sum_{\substack{\mu R \\ \nu R'}} C_{\mu\alpha}^*(k) C_{\nu\alpha}(k) e^{-ik(R-R')} A_{\mu R, \nu R'}^\Sigma \right., \tag{8.6}$$

$$\Delta E^{(2)} = [\text{expression (6.6) with } V \text{ substituted by } W].$$

The notation of Sec. VI is used here. Matrix A, as introduced by (8.6), has the diagonal block structure

$$A = \left(\begin{array}{c|c} A^M & 0 \\ \hline 0 & A^\Sigma \end{array} \right)$$

and is evaluated as $A = WsS_0^{-1} + S_0^{-1}sW$. Its elements are explicitly given in Appendix B, Eq. (B11).

The projected Green's matrices of Sec. VI needed to calculate $\Delta E^{(2)}$ are defined as in Eq. (6.5), with the Bloch MO coefficients and energies satisfying Eq. (8.1). The same is true of the MO coefficients and energies of the adsorbate molecule.

Evaluating matrices W, Eq. (8.5) and A, Eq. (B11) poses no serious problems. Although S_0 corresponds to an extended system, V and s are well localized, so the corresponding matrix multiplications converge rapidly.

The new term $\Delta E^{(1)}$ is an exchange repulsion energy. This contribution, typical in perturbation expansions using nonorthogonal AOs, is well known in the usual theory of intermolecular interactions.[16,17] In application to adsorption problems it has been mentioned in Ref. 7 and 18, but the explicit form (8.6) seems to be a new result. van Santen and co-workers have used perturbation-theory based expressions that include overlap.[7b,c,e,18]

IX. DISCUSSION

(a) In the present paper we apply the perturbation expansions (1.10) and (5.3), derived from consideration of the Einstein–Schrieffer theory,[10] to a study of the interaction energy in typical extended systems. Operating with the basic formula (5.3) involves a rather unusual technique of calculating the imaginary part of traces over matrix products.

In the second order of Hückel theory the result appears as formulas (5.6), (5.9), and (6.6) which are nothing else than different continuum reformulations of a trivial second-order interaction energy, known from molecular quantum

chemistry. However, higher-order expressions are readily available by the same technique. This may be helpful, for instance, in analyzing through-surface interactions of adsorbate molecules which, as indicated in Sec. VI, appear only in fourth order. The corresponding numerical analysis of closed nonperturbational energy expressions for simple chemical systems has been reported (see Refs. 10 and 15). This preliminary consideration showed an oscillatory behavior of the corresponding secondary interactions as a function of the relative positions of interacting molecules. This is quite understandable from the point of view of the present perturbational treatment, because the related energy contributions will arise as a combination of Green's functions of type (6.5) with nonvanishing factors $\exp[\pm ik(R - R')]$.

(b) Expression (6.6) [or its EH counterpart (8.6)] can serve as a basis for a qualitative adsorption theory when net charge distribution effects are negligible. The projected Green's functions $G_{\mu\nu}^{\pm}(E, R - R')$, as introduced in Eq. (6.5), provide a natural measure of relative reactivity of different surface positions in both Hückel and EH treatments. They are closely related to the bond–bond polarizabilities introduced by Coulson and Longuet-Higgins.[3] These surface reactivity indices can be evaluated for a given surface model by conventional techniques of band structure calculation, with no more computational effort than that needed for DOS calculations. An alternative procedure, based on formula (7.5), implies straightforward derivation of projected Green's functions from the local DOS matrix.

(c) A phenomenological treatment of adsorption energies can be derived starting from formula (7.5), if some simple model is taken for local DOS's. This kind of approach originally used formula (5.4) (with electrostatic interaction added) and introduced both $n(E)$ and $n_0(E)$ in an empirical manner.[19] In later work a perturbational formula of type (5.6) was applied.[6] For the adsorption case, with the notation of Sec. VI this formula reads

$$\Delta E = \frac{2}{\Omega} \left\{ \sum_{i(\epsilon_i < \epsilon_F)} \int_{\epsilon_F}^{\infty} n_0(E')dE' \frac{|\langle\epsilon_i|V|E'\rangle|^2}{\epsilon_i - E'} \right.$$
$$\left. - \sum_{i(\epsilon_i > \epsilon_F)} \int_{-\infty}^{\epsilon_F} n_0(E')dE' \frac{|\langle\epsilon_i|V|E'\rangle|^2}{\epsilon_i - E'} \right\} \quad (9.1)$$

(the interaction matrix elements are assumed to be r,s-independent here). The phenomenology of operating with formula (9.1) needs independent assumptions of the energy dependence of two quantities: the DOS $n_0(E')$, and the matrix elements $\langle\epsilon_i|V|E'\rangle$. However, only modeling of the DOS is needed when formula (7.5) is applied, because, according to Eq. (6.6), all the energy dependences are cumulated in projected Green's functions. This seems to offer a significant conceptual advantage.

Tentative calculations with a rectangular form of the DOS applied in Eq. (7.5) give the same result as reported earlier[6] and obtained using Eq. (9.1), with an additional assumption $\langle\epsilon_i|V|E'\rangle$ = const. The coincidence of the results shows that actually this latter assumption is a mathematical consequence of the rectangular DOS model. Hence it need not be introduced as a special condition. The further

development of the present approach with more sophisticated DOS models seems promising.

APPENDIX A: QUALITATIVE DISCUSSION OF THE ENERGY SPECTRUM OF A LATTICE BUILT OF A PAIR OF WEAKLY INTERACTING SUBLATTICES

Let the $n_0(E)$ spectrum be constituted of a pair of well-separated sharp peaks $n_1(E)$ and $n_2(E)$, [Not to be confused with first- and second-order corrections $n^{(1)}$ and $n^{(2)}$.] located around points E_1 and E_2 (Fig. 1):

$$n_0(E) = n_1(E) + n_2(E) \quad E_2 > E_1. \quad (A1)$$

This form of spectrum implies that Eq. (3.4) is true. We use approximate formula (3.11), neglecting for brevity the r,s dependence of interaction matrix elements. In this treatment

$$\frac{R(E,E')}{E - E'} = \frac{|\langle E|V|E'\rangle|^2}{E - E'}$$

is supposed to be a smooth function of E', E, since the pole at $E = E'$ is eliminated by the condition (3.4). All we need to evaluate the integral

$$\int dE' n_0(E') \frac{|\langle E|V|E'\rangle|^2}{E - E'} \quad (A2)$$

are the values of the integrand near $E = E_1$ and $E = E_2$:

$$n_0(E') \frac{|\langle E|V|E'\rangle|^2}{E - E'}$$
$$\cong \begin{cases} n_1(E') \dfrac{|\langle E_2|V|E_1\rangle|^2}{E_2 - E_1} & \text{near } E = E_1 \\[2mm] n_2(E') \dfrac{|\langle E_1|V|E_2\rangle|^2}{E_1 - E_2} & \text{near } E = E_2 \end{cases} \quad (A3)$$

Inserting this in Eq. (3.11), we obtain

$$n(E) \cong \begin{cases} n_1(E) - \dfrac{a}{2}\dfrac{d}{dE}n_1(E) & \text{near } E = E_1 \\[2mm] n_2(E) - \dfrac{b}{2}\dfrac{d}{dE}n_2(E) & \text{near } E = E_2 \end{cases}, \quad (A4)$$
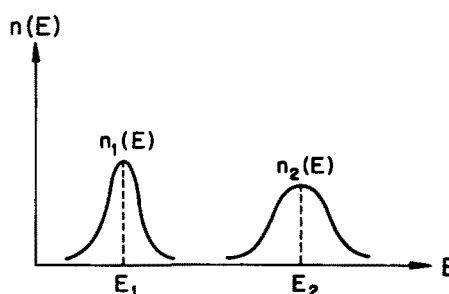
where

FIG. 1. Schematic representation of the zeroth approximation DOS. $n_1(E)$ and $n_2(E)$ are DOS's of noninteracting sublattices.

$$a = \frac{|\langle E_1|V|E_2\rangle|^2}{E_1 - E_2} \int dE' n_2(E') < 0,$$

$$b = \frac{|\langle E_2|V|E_1\rangle|^2}{E_2 - E_1} \int dE' n_1(E') > 0. \qquad (A5)$$

Now we write expansions of (A4) near E_1 and E_2:

$$n_1(E) = \text{const} - \tfrac{1}{2} k_1 (E - E_1)^2;$$

$$\frac{dn_1}{dE} = - k_1 (E - E_1),$$

$$n_2(E) = \text{const} - \tfrac{1}{2} k_2 (E - E_2)^2;$$

$$\frac{dn_2}{dE} = - k_2 (E - E_2).$$

The shifts of the maxima of the function (A4) are given by

$$E_{\text{max}} - E_1 = \frac{1}{2} \frac{a}{2} < 0 \quad (\text{near } E = E_1),$$

$$E_{\text{max}} - E_2 = \frac{1}{2} \frac{b}{2} > 0 \quad (\text{near } E = E_2). \qquad (A6)$$

So the interaction moves apart the band maxima, lowering the lower one and raising the higher one. This is the picture intuitively expected by analogy with the standard perturbation analysis of discrete molecular systems.

APPENDIX B: THE EH TREATMENT IN DETAIL

A. Tensorial formulation of EH theory

In order to calculate the traces entering the main perturbational formula (5.3), we use tensorial notations which allow one to write all equations in a covariant (= basis independent) form.[20] The following conventions apply:

(i) Matrices of operators are associated with covariant tensors: $H_{0\mu\nu}$, $G_{0\mu\nu}$, $V_{\mu\nu}$.

(ii) Column eigenvectors are associated with contravariant vectors: C^μ, whereas eigenvalues are considered as scalar numbers (ϵ_0).

(iii) The covariant and contravariant metric tensors $g_{\mu\nu}$ and $g^{\mu\nu}$ are associated with the overlap matrix S and its inverse S^{-1}, respectively; in the zeroth approximation these reduce to S_0 and S_0^{-1}.

To give an illustration, let us derive secular equation (8.1) using tensorial notations. The covariant version of this equation is defined uniquely by the above rules as

$$H_{0\mu\nu} C^\nu = g_{\mu\nu} C^\nu \epsilon_0. \qquad (B1)$$

The metric tensor on the right-hand side is needed in order to make both sides of Eq. (B1) vectors of the same (covariant) type. The matrix transcription of this equation, as obtained according to the above rules, is as needed:

$$H_0 C = S_0 C \epsilon. \qquad (B2)$$

Applying these rules to derive the covariant prescriptions for matrix multiplication and trace evaluation operations, we obtain for a pair of matrices A, B:

Orthogonal basis	tensorial notation	nonorthogonal basis
AB	$A_{\mu\nu} g^{\nu\lambda} B_{\lambda\rho}$	$AS^{-1}B$
tr AB	$A_{\mu\nu} g^{\nu\lambda} B_{\lambda\rho} g^{\rho\mu}$	tr$(AS^{-1}BS^{-1})$

The first- and second-order energy correction [following from general expression (5.3)] will then be

$$\Delta E = - \frac{2}{\pi\Omega} \text{Im} \int_{-\infty}^{\epsilon_F} \{ \text{tr}[G_0 S^{-1} V S^{-1}]$$

$$+ \frac{1}{2} \text{tr}[G_0 S^{-1} V S^{-1}]^2 \} dE. \qquad (B3)$$

B. Utilization of the block structure of matrices

The overlap matrix is subdivided into intra- and inter-subsystem parts according to

$$S = S_0 + s. \qquad (B4)$$

We consider s as a perturbation, as well as the interaction matrix V. Then the calculation of S^{-1} with the needed accuracy gives

$$S^{-1} = S_0^{-1} - S_0^{-1} s S_0^{-1} \qquad (B5)$$

The matrices needed to calculate Eq. (B3) have the following block structure (see Sec. VI):

$$G_0 = \begin{pmatrix} G^M & O \\ \hline O & G^\Sigma \end{pmatrix}; \quad S_0 = \begin{pmatrix} S^M & O \\ \hline O & S^\Sigma \end{pmatrix} \qquad \textbf{(type I)}$$

$$V = \begin{pmatrix} O & \boxed{} \\ \hline \boxed{} & O \end{pmatrix}; \quad s = \begin{pmatrix} O & \boxed{} \\ \hline \boxed{} & O \end{pmatrix} \qquad \textbf{(type II)}$$

The matrices having diagonal and off-diagonal block structures will be further referred to as "type I" and "type II" matrices, respectively. The following two symbolic rules determine the change of the matrix type under matrix multiplication:

$$I \cdot II = II \cdot I = II,$$

$$I \cdot I = II \cdot II = I, \qquad (B6)$$

$$\text{tr } II = 0.$$

The latter rule greatly simplifies the trace calculation. Now we substitute Eq. (B5) into Eq. (B3) and calculate traces using Eq. (B6) to obtain

$$\text{tr}(G_0 S^{-1} V S^{-1}) = - \text{tr} G_0 A$$

$$\tfrac{1}{2} \text{tr}(G_0 S^{-1} V S^{-1})^2 = \tfrac{1}{2} \text{tr}(G_0 W)^2, \qquad (B7)$$

where

$$A = S_0^{-1} V S_0^{-1} s S_0^{-1} + S_0^{-1} s S_0^{-1} V S_0^{-1}$$

$$= W s S_0^{-1} + S_0^{-1} s W \qquad (B8)$$

$$W = S_0^{-1} V S_0^{-1}.$$

Note that A and W are real Hermitian matrices and according to Eq. (B6) A is of type I and W is of type II:

$$A = \begin{pmatrix} A^M & O \\ \hline O & A^\Sigma \end{pmatrix} \quad W = \begin{pmatrix} O & \boxed{} \\ \hline \boxed{} & O \end{pmatrix}$$

So the energy is obtained in the form

$$\Delta E = \Delta E^{(1)} + \Delta E^{(2)},$$

$$\Delta E^{(1)} = \frac{2}{\pi \Omega} \operatorname{Im} \int_{-\infty}^{\epsilon_F} dE \operatorname{tr} G_0 A, \qquad (B9)$$

$$\Delta E^{(2)} = -\frac{1}{\pi \Omega} \operatorname{Im} \int_{-\infty}^{\epsilon_F} dE \operatorname{tr}(G_0 W)^2.$$

Next we use G_0 in the form (8.4) and calculate Im following the technique of Secs. V and VI.

C. Calculation of $\Delta E^{(1)}$

As mentioned in Sec. V, the complex nature of C can be ignored when calculating Im. Let us demonstrate how this general rule works in the $\Delta E^{(1)}$ calculation:

$$\operatorname{tr}(G_0 A) = \operatorname{tr}\{C [(E + i\delta)I - \epsilon]^{-1} C^\dagger A\}$$

$$= \operatorname{tr}\{[(E + i\delta)I - \epsilon]^{-1} C^\dagger A C\}$$

$$= \sum_i \frac{1}{E + i\delta - \epsilon_i} [C^\dagger A C]_{ii}.$$

The matrix $C^\dagger A C$ is Hermitian, so its diagonal elements are real. Hence only the first factor in Σ_i should be counted as a complex quantity in the Im calculation.

In evaluation of $\Delta E^{(1)}$ we need block structures:

$$C = \left(\begin{array}{c|c} C^M & 0 \\ \hline 0 & C^\Sigma \end{array} \right); \quad \epsilon = \left(\begin{array}{c|c} \epsilon^M & 0 \\ \hline 0 & \epsilon^\Sigma \end{array} \right).$$

So we obtain

$$\Delta E^{(1)} = -\frac{2}{\Omega} \int_{-\infty}^{\epsilon_F} dE \operatorname{tr}[\delta(E - \epsilon^M) C^{M\dagger} A^M C^M$$

$$+ \delta(E - \epsilon^\Sigma) C^{\Sigma\dagger} A^\Sigma C^\Sigma].$$

Utilization of notations introduced in Sec. VI gives finally

$$\Delta E^{(1)} = -\frac{2}{\Omega} \left\{ \sum_{i(\epsilon_i < \epsilon_F)} \sum_{rs} C_{ri} C_{si} A_{rs}^M \right.$$

$$+ \frac{1}{N} \sum_\alpha \int \frac{dk}{(2\pi)^2} \vartheta [\epsilon_F - \epsilon_\alpha(k)]$$

$$\left. \times \sum_{\substack{\mu R \\ vR'}} C_{\mu\alpha}^*(k) C_{v\alpha}(k) e^{-ik(R - R')} A_{\mu R, vR'}^\Sigma \right\} \qquad (B10)$$

where

$$A_{rs}^M = \sum_{t,\mu R} W_{r,\mu R} S_{\mu R,t} S_{0\ ts}^{-1} + S_{0\ rt}^{-1} S_{t,\mu R} W_{\mu R,s}$$

$$= \sum_{t,\mu R} (W_{r,\mu R} S_{0\ ts}^{-1} + S_{0\ rt}^{-1} W_{s,\mu R}) S_{t,\mu R}$$

$$A_{\mu R, vR'}^\Sigma = \sum_{t,\lambda R''} (W_{\mu R,t} S_{t,\lambda R''} S_{0\ \lambda R'',vR'}^{-1}$$

$$+ S_{0\mu R,\lambda R''}^{-1} S_{\lambda R'',t} W_{t,vR'})$$

$$= \sum_{t,\lambda R''} (W_{t,\mu R} S_{0\ \lambda R'',vR'}^{-1} + S_{0\ \mu R,\lambda R''}^{-1} W_{t,vR'}) S_{t,\lambda R''} \qquad (B11)$$

with W given by Eq. (B8).

D. Calculation of $\Delta E^{(2)}$

We observe that the only difference between $\Delta E^{(2)}$ in Eq. (B9) and ΔE in (6.2) is the substitution of V by W.

These latter matrices have the same structure, so we can immediately use the result (6.6).

APPENDIX C: CALCULATION OF PROJECTED GREEN FUNCTIONS FOR A ONE-DIMENSIONAL CHAIN AS AN EXAMPLE

For a chain with equal interatomic distances l we have two parameters: l and the corresponding resonance integral β. We take $\alpha = \epsilon_F = 0$. Then [The Green's functions are multiplied by N (the number of unit cells) in this Appendix. The unnecessary (for this particular case) subscripts are also omitted: $G_{00}^{\pm}(E,nl) \to G^{\pm}(E,nl) \to G^{\pm}(E,n)$]

$$G^-(E,nl) = 2 \int_0^{\pi/2l} \frac{\cos nkl}{E - 2\beta \cos kl} \frac{dk}{2\pi} \quad (E > 0)$$

$$G^+(E,nl) = 2 \int_{\pi/2l}^{\pi/l} \frac{\cos nkl}{E - 2\beta \cos kl} \frac{dk}{2\pi} \quad (E < 0) \qquad (C1)$$

Here $R - R' = nl$. We introduce new variables $z = E/2|\beta|$ and $n = (R - R')/l$ in terms of which the function $G^{\pm}(z, n = 0)$ and $G^{\pm}(z, n = 1)$ are easily evaluated. The result for the diagonal functions ($n = 0$) is

For $z^2 < 1$:

$$(2l|\beta|)G^-(z,0)$$

$$= \frac{1}{\pi} \frac{1}{\sqrt{1 - z^2}} \ln \left| \frac{\sqrt{1 - z} + \sqrt{1 + z}}{\sqrt{1 - z} - \sqrt{1 + z}} \right| \quad (z > 0),$$

$$(2l|\beta|)G^+(z,0)$$

$$= \frac{1}{\pi} \frac{1}{\sqrt{1 - z^2}} \ln \left| \frac{\sqrt{1 - z} - \sqrt{1 + z}}{\sqrt{1 - z} + \sqrt{1 + z}} \right| \quad (z < 0).$$
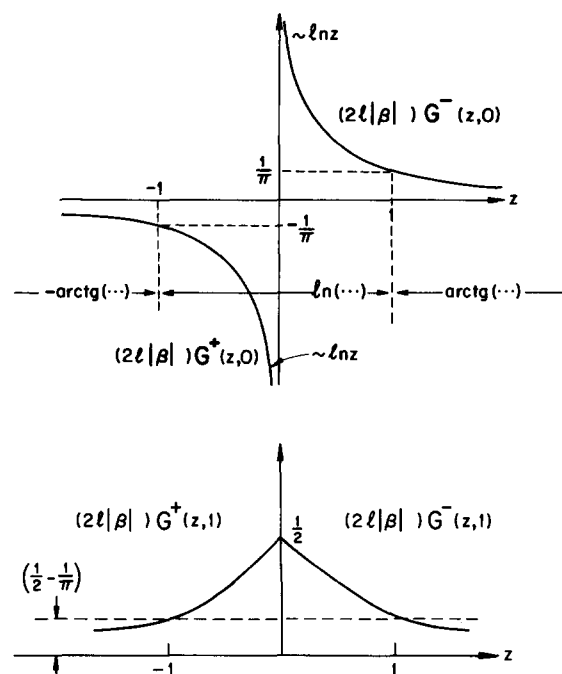

FIG. 2. The diagonal and the first off-diagonal projected Green's functions for an infinite polyene chain in the Hückel method.

For $z^2 > 1$

$(2l|\beta|)G^-(z,0)$

$= \dfrac{2}{\pi} \dfrac{1}{\sqrt{z^2-1}} \arctan \sqrt{\dfrac{z-1}{z+1}} \quad (z>0),$

$(2l|\beta|)G^+(z,0)$

$= -\dfrac{2}{\pi} \dfrac{1}{\sqrt{z^2-1}} \arctan \sqrt{\dfrac{z+1}{z-1}} \quad (z<0).$

The off-diagonal Green's functions ($n = 1$) are

$(2l|\beta|)G^-(z,1) = -z(2l|\beta|)G^-(z,0) + \tfrac{1}{2} \quad (z>0),$

$(2l|\beta|)G^+(z,1) = -z(2l|\beta|)G^+(z,0) + \tfrac{1}{2} \quad (z<0).$

These formulas are illustrated by Fig. 2. The diagonal Green's functions are smooth, except for the logarithmic divergence at the Fermi level. The off-diagonal Green's functions have a logarithmically divergent first derivative at the Fermi level. The divergency points to a breakdown of the perturbation theory and seems to be a general rule.

Some other general properties of the quantities $G^{\pm}(E,nl)$ (C.1) can also be established. They follow from the fact that the denominator of their integrands is a monotonic function within the integration interval. The consequences are, first, that the absolute value of a Green's function decreases at fixed E when n increases, and, second, that its sign is uniquely determined by the sign which the cosine in the numerator takes in the vicinity of Fermi level $k = \pi/2$. There exists also an obvious symmetry relation,

$G^+(-E,nl) = (-1)^{n+1} G^-(E,nl).$

[1] K. Fukui, Science 218, 747 (1982) and references therein.
[2] T. A. Albright, J. K. Burdett, and M.-H. Whangbo, Orbital Interactions in Chemistry (Wiley, New York, 1985).
[3] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. A191, 39 (1947); A192, 16 (1947); A193, 447 (1948).
[4] M. J. S. Dewar, J. Amer. Chem. Soc. 74, 3341 (1952).
[5] R. Hoffmann, Rev. Mod. Phys. 60, 601 (1988); R. Hoffmann, Solids and Surfaces: A Chemist's View of Bonding in Extended Structures (VCH, New York, 1988) and references therein.
[6] E. Shustorovich, Solid State Commun. 44, 567 (1982); E. Shustorovich, R. C. Baetzold, and E. L. Muetterties, J. Phys. Chem. 87, 1100 (1983); E. Shustorovich, Surf. Sci. 163, L730 (1985).
[7] (a) R. A. van Santen, Progr. Surf. Sci. 25, 253 (1987) and references therein; (b) R. A. van Santen, J. Chem. Soc. Faraday Trans. 1, 83, 1915 (1987); (c) R. A. van Santen, J. Mol. Struct. 173, 157 (1988); (d) R. A. van Santen, J. Mol. Catal. 54, 157 (1989); (e) R. A. van Santen and A. de Koster in "New Trends in CO Activation", edited by L. Guczi, in press; (f) For an early utilization of a Green's function formalism in chemisorption theory see R. A. van Santen and L. H. Toneman, Int. J. Quantum Chem. 12 (Suppl. 2), 83 (1977); (g) R. A. van Santen and E. J. Baerends, in Theoretical Models of Chemical Bonding, Part IV, edited by Z. B. Maksic (Springer, Berlin), in press.
[8] A. Imamura, Y. Aoki, S. Suhai, J. Ladik, J. Chem. Phys. 83, 5727 (1985).
[9] W. Jones and N. H. March, Theoretical Solid State Physics (Wiley, London, 1973), Vol. 1.
[10] T. L. Einstein and J. R. Schrieffer, Phys. Rev. B7, 3629 (1973).
[11] V. Heine, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnball (Academic, New York, 1980), Vol. 35, Chap. 1.
[12] R. Bellman, Introduction to Matrix Analysis (McGraw-Hill, New York, 1970), p. 100.
[13] R. G. Newton, Scattering Theory of Waves and Particles (McGraw-Hill, New York, 1966).
[14] N. W. Ashcroft, N. D. Mermin, Solid State Physics (Holt, Rinehart, Winston, 1976).
[15] T. B. Grimley, Proc. Roy. Soc. 90, 751 (1967); T. B. Grimley, S. M. Walker, Surf. Sci. 14, 395 (1969).
[16] L. Salem, J. Amer. Chem. Soc. 90, 543 (1968).
[17] M. V. Basilevsky, Theor. Chim. Acta (Berl.) 13, 409 (1969); M. V. Basilevsky and M. M. Berenfeld, Intern. J. Quant. Chem. 6, 555 (1972).
[18] A. de Koster, A. P. J. Jansen, J. J. C. Geerlings, and R. A. van Santen (to be published).
[19] C. M. Varma and A. J. Wilson, Phys. Rev. B22, 3795, 3805 (1980); W. Andreoni, C. M. Varma, Phys. Rev. B23, 437 (1981).
[20] I. S. Sokolnikoff, Tensor Analysis (Wiley, New York, 1951).