

Covalent effects in the effective-medium theory of chemical binding: Hydrogen heats of solution in the 3d metals

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The effective-medium-theory estimate of the binding energy of an atom to a host (another atom, molecule, or solid) from the host electron density, and the binding energy of the atom in a homogeneous electron gas has been extended to include covalent effects. The covalent term involves the difference in the one-electron energies between the atom in the host and the atom in homogeneous electron-gas systems. The scheme is tested for helium impurities in several transition metals and for hydrogen impurities in all the metals from potassium to copper. For helium all available binding energies are well reproduced and all the observed trends in the hydrogen heat of solution can be accounted for.

I. INTRODUCTION

Along with the increasing ability to successfully predict or confirm the binding properties of molecules and solids from first-principles calculations,¹ there is a search for simpler methods. There are two main motivations. First, the first-principles calculations are so time consuming, in particular when the symmetry is low, that there is little hope at present that the great number of different systems of interest in, for instance, surface physics can be treated. A scheme that makes predictions possible on the basis of a knowledge of the properties of only the constituent atoms, molecules, and solids is needed. In conjunction with this, the second motivation is that simple schemes, by definition, must single out the essential parameters of the problem. Finding a simple scheme, therefore, often reveals some of the underlying physics of the problem. Examples include the work of Pettifor² and that of Williams, Gelatt, and Moruzzi³ explaining the trends in the transition-metal alloy heats of formation, and the efforts of Varma and Wilson⁴ and Muscat and News⁵ to explain the trends in chemisorption energies.

Another simple approach is the effective-medium theory proposed by Stott and Zaremba⁶ and Nørskov and Lang⁷ for calculating the embedding energy of an atom in a host system (a bulk solid, a surface or another atom or molecule). The basic idea is to replace the (low-symmetry) host by an effective (high-symmetry) host consisting of a homogeneous electron gas of a density equal to that seen by the atom. The embedding energy ΔE ,

defined as the energy difference between the combined atom and host system minus that of the separated atom and host, is thus given by

$$\Delta E(\vec{r}) = \Delta E^{\text{hom}}(n_0(\vec{r})), \quad (1.1)$$

where $\Delta E^{\text{hom}}(n_0)$ is the energy of the atom in a homogeneous electron gas (jellium) of density n_0 , and $n_0(\vec{r})$ is the host electron density at the site \vec{r} of the atom. The only parameter characterizing the host is $n_0(\vec{r})$, and the properties of the atom are given by the function $\Delta E^{\text{hom}}(n_0)$, which can be calculated once and for all for each atom. This has now been done within the local density approximation for all the atoms from H to Ar by Puska *et al.*⁸ A number of these results are shown in Fig. 1.

Two classes of ΔE^{hom} curves are seen: the rare gases and all the others. For the former, ΔE^{hom} rises monotonically (linearly) with n_0 , indicating the well-known fact that these atoms will interact repulsively with any host. The rise in energy is simply due to the kinetic energy repulsion between the host and atomic electrons. This repulsion is stronger the more atomic states the host states must orthogonalize to. For the other atoms, a minimum is seen in ΔE^{hom} signifying the reactivity of these open-shell atoms. As for the rare gases the repulsive part of ΔE^{hom} is governed by the kinetic energy repulsion. The attraction is given by the gain in energy when electrons are transferred from the electron gas to the affinity level of the atom [$\Delta E^{\text{hom}}(0) = -A$, where A is the atomic affinity] and by the subsequent screening of the extra atomic electrons.⁶ As shown, for instance, by Pus-

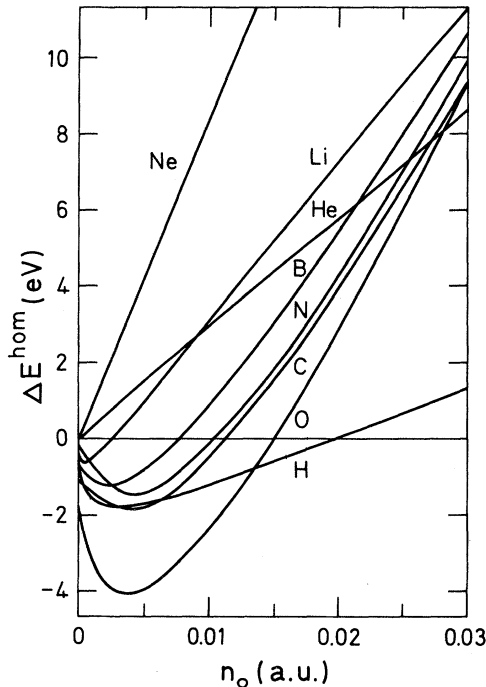


FIG. 1. Embedding energies of He, H, Li, B, N, C, O, and Ne in a homogeneous electron gas (jellium) as a function of electron-gas density (from Ref. 8).

ka *et al.*,⁸ the depth of the minimum in $\Delta E^{\text{hom}}(n_0)$ correlates very well with typical bond strengths of the atom in question.

In some of the few cases where first-principles calculations of binding energies exist, the simple estimate of Eq. (1.1) has been tested. This is the case for the chemisorption energies of both hydrogen and oxygen outside jellium surfaces and for the helium trapping energies in jellium vacancies. Good agreement is found for both the size of the binding energies and the bond lengths, considering the simplicity of the approach.^{6,7}

The simple picture behind Eq. (1.1) can be improved by considering the deviation of the host density $n_0(\vec{r})$ from homogeneity in perturbation theory.⁶ The first-order correction to Eq. (1.1) is⁷

$$\Delta E^{(1)}(\vec{r}) = \int \Delta\rho(|\vec{r}' - \vec{r}|) \delta v^{\text{ext}}(\vec{r}') d\vec{r}', \quad (1.2)$$

where $\Delta\rho(r) = \Delta n(r) - Z\delta(\vec{0})$ is the atom-induced charge density (including the nuclear charge Z) in the homogeneous electron gas, and δv^{ext} is the difference in external potential between the real host and the effective medium. If, instead of using $n_0(\vec{r})$ in Eq. (1.1), we use an average density $\bar{n}_0(\vec{r})$ defined by^{6,7}

$$\bar{n}_0(\vec{r}) = \frac{\int \Delta\phi(|\vec{r}' - \vec{r}|) n_0(\vec{r}') d\vec{r}'}{\int \Delta\phi(r') d\vec{r}'}, \quad (1.3)$$

where

$$\Delta\phi(r) = \int \frac{\Delta\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

is the atom-induced electrostatic potential in the homogeneous electron gas, then Eq. (1.2) can be written as follows^{6,7}:

$$\Delta E^{(1)}(\vec{r}) = \int \Delta\rho(|\vec{r}' - \vec{r}|) \phi_0(\vec{r}) d\vec{r}'. \quad (1.4)$$

Here

$$\phi_0(\vec{r}) = \int \frac{\rho_0(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

is the host electrostatic potential. Including the first-order correction for, e.g., the chemisorption energies of hydrogen and oxygen outside jellium surfaces, makes the difference between the effective-medium estimate and the first-principles calculations even smaller.⁷

The basis for the perturbation theory is that, due to screening, the atomic charge density $\Delta\rho$ is so localized that even though, e.g., ϕ_0 in Eq. (1.4) may change strongly far from the atom, it only varies little over the region where $\Delta\rho$ is appreciable. This does present a problem though. It is true that the main part of $\Delta\rho$ is localized in the close vicinity of the nucleus, but the Friedel oscillations in the electron density only decay slowly with distance. The oscillations are only a small part of $\Delta\rho$ and, if no strong scattering centers exist in the host, there will be no problem, as indicated by the success of the simple form Eq. (1.4) outside and in jellium. In general, however, the core regions of the host atoms have very large variations in the electrostatic potential ϕ_0 and even though $\Delta\rho$ is small the first-order term is bound to give an unrealistically large contribution.

It is the purpose of this paper to treat this problem. It is solved by restricting the region in space where the deviations of the host from homogeneity are assumed small to the close vicinity of the atom. Outside this region, the host potential is treated to infinite order. Here, on the other hand, the atom can be regarded as the small perturbation. With such a mixed perturbation theory, the first-order term, Eq. (1.4), is refound with all integrals over the atomic region only. The outside region gives rise to a new term in addition to Eq. (1.4). This term can be considered as representing the covalent interactions between the atom and the host. The

new version of the effective-medium theory is presented in Sec. II. Then, in Sec. III, the scheme is applied to a number of systems. The main example is the evaluation of the hydrogen heats of solution in all the metals from K to Cu. It is shown that the most important factor responsible for the observed large variations in the heats of solution along the row is the variations in the interstitial electron density through the zeroth-order term, Eq. (1.1). Finally, in Sec. IV, the prospects for and some of the problems with the method are discussed.

II. THEORY

Following Hohenberg and Kohn,⁹ the total energy of a system with electron density $n(\vec{r})$ can be written

$$E[n] = T[n] + G[n] + E_{NN}, \quad (2.1)$$

where $T[n]$ is the kinetic energy of a noninteracting electron system of density $n(\vec{r})$, E_{NN} is the internuclear interaction, and

$$G[n] = \frac{1}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + \int v^{\text{ext}}(\vec{r})n(\vec{r})d\vec{r} + E_{\text{xc}}[n] \quad (2.2)$$

is the sum of the average Coulomb interaction between the electrons, the interaction with the external potential (the nuclei), and the exchange and correlation energy. In the local density approximation the latter is given by¹⁰

$$E_{\text{xc}}[n] = \int n(\vec{r})\epsilon_{\text{xc}}^{\text{hom}}(n(\vec{r}))d\vec{r}, \quad (2.3)$$

where $\epsilon_{\text{xc}}^{\text{hom}}(n)$ is the exchange-correlation energy density in a homogeneous electron gas of density n . In this approximation, a local, effective potential $v(\vec{r})$ can be defined as follows:

$$v(\vec{r}) = \frac{\delta G[n]}{\delta n(\vec{r})}, \quad (2.4)$$

so that the ground-state density $n(\vec{r})$ can be found by solving a set of one-electron Schrödinger equations self-consistently:

$$\left[-\frac{1}{2}\nabla^2 + v(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}), \quad (2.5)$$

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2. \quad (2.6)$$

The eigenvalues ϵ_i in Eq. (2.5) do not have any *a priori* physical meaning, but we note that the kinetic energy term $T[n]$ can be expressed through them as

$$T[n] = \sum_i \epsilon_i - \int n(\vec{r})v(\vec{r})d\vec{r}. \quad (2.7)$$

Slightly generalizing the problem stated in the Introduction, the main purpose of the effective-medium theory is to calculate the change in energy of an atom A , when it is moved from one host B to another \tilde{B} . The embedding energy of the atom in B , $\Delta E = E - E^0$, is the difference between the total energy E of the combined system A in B , and the energy E^0 of the separated atom and host. Similarly, $\Delta\tilde{E} = \tilde{E} - \tilde{E}^0$ is the embedding energy in \tilde{B} and the embedding energy change is

$$\begin{aligned} \delta\Delta E &= \Delta\tilde{E} - \Delta E = (\tilde{E} - E) - (\tilde{E}^0 - E^0) \\ &= \delta E - \delta E^0. \end{aligned} \quad (2.8)$$

Here and throughout, a tilde denotes a quantity in system \tilde{B} , whereas a superscript 0 denotes the system without the atom (the bare host). Furthermore, a δ denotes a difference between \tilde{B} and B , and a Δ indicates a difference between the system with and without the atom.

The usual situation is that we know ΔE and want $\Delta\tilde{E}$. The effective medium B is then chosen to resemble \tilde{B} as much as possible in the region close to the atom. We can then hope to be able to treat $\delta\Delta E$ in perturbation theory. To do this we divide space up into a region a close to the atom, and a region b outside. Owing to the choice of B , the potential v_a in region a will not be very different in B and \tilde{B} . To first order in the density change δn_a , when A is moved from B to \tilde{B} , we can simply assume $\tilde{v}_a = v_a$ and $\tilde{v}_a^0 = v_a^0$. In region b , on the other hand, the potential is dominated by the host. Here it is the influence of the atom which is small. In insulators this is due to the localized nature of the atomic states and in metallic hosts it is due to screening. To first order in the atom-induced density Δn_b in region b we can thus assume $\tilde{v}_b = \tilde{v}_b^0$ and $v_b = v_b^0$. If $\delta\Delta E$ is calculated using the following assumptions:

$$\begin{aligned} \tilde{v}_a &= v_a, \quad \tilde{v}_a^0 = v_a^0, \\ \tilde{v}_b &= \tilde{v}_b^0, \quad v_b = v_b^0, \end{aligned} \quad (2.9)$$

it will be good to first order in the difference between B and \tilde{B} in region a , where the atom dominates, and to first order in the influence of the atom in region b , where the host dominates.

In the following we consider contributions of the two terms T and G in Eqs. (2.7) and (2.2) to δE and δE^0 , and to $\delta\Delta E$ [Eq. (2.8)] separately. From Eq. (2.7) it is seen that

$$\delta T = \delta \left[\sum \epsilon_i \right] - \int_a \tilde{v}_a(\vec{r}) \tilde{n}_a(\vec{r}) d\vec{r} - \int_b \tilde{v}_b(\vec{r}) \tilde{n}_b(\vec{r}) d\vec{r} + \int_a v_a(\vec{r}) n_a(\vec{r}) d\vec{r} + \int_b v_b(\vec{r}) n_b(\vec{r}) d\vec{r}.$$

Similarly, we have

$$\delta T^0 = \delta \left[\sum \epsilon_i^0 \right] - \int_a \tilde{v}_a^0(\vec{r}) \tilde{n}_a^0(\vec{r}) d\vec{r} - \int_b \tilde{v}_b^0(\vec{r}) \tilde{n}_b^0(\vec{r}) d\vec{r} + \int_a v_a^0(\vec{r}) n_a^0(\vec{r}) d\vec{r} + \int_b v_b^0(\vec{r}) n_b^0(\vec{r}) d\vec{r}.$$

With the use of the approximations in Eq. (2.9) this gives

$$\begin{aligned} \delta \Delta T = \delta T - \delta T_0 = \delta \Delta \left[\sum \epsilon_i \right] - \int_a v_a(\vec{r}) \delta n_a(\vec{r}) d\vec{r} + \int_a v_a^0(\vec{r}) \delta n_a^0(\vec{r}) d\vec{r} - \int_b \tilde{v}_b^0(\vec{r}) \Delta \tilde{n}_b(\vec{r}) d\vec{r} \\ + \int_b v_b^0(\vec{r}) \Delta n_b(\vec{r}) d\vec{r}. \end{aligned} \quad (2.10)$$

In order to evaluate $\delta \Delta G + \delta \Delta E_{NN}$, we note that in the local density approximation, Eq. (2.2) can be written as follows:

$$G[n] + E_{NN} = (G[n_a] + E_{NN}^a) + (G[n_b] + E_{NN}^b) + \int_a \int_b \frac{\rho_a(\vec{r}) \rho_b(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'. \quad (2.11)$$

Here $G[n_a]$ stems from the electrons in region a only, E_{NN}^a is the internuclear interaction within a , and $\rho_a(\vec{r}) = n_a(\vec{r}) - \sum_n Z_n \delta(\vec{r} - \vec{R}_n)$ is the total charge density within region a . The change in $G + E_{NN}$ is

$$\begin{aligned} \delta G + \delta E_{NN} &= G[\tilde{n}] - G[n] + \tilde{E}_{NN} - E_{NN} \\ &= G[\tilde{n}_a] - G[n_a] + G[\tilde{n}_b] - G[n_b] + \tilde{E}_{NN}^a - E_{NN}^a + \tilde{E}_{NN}^b - E_{NN}^b \\ &\quad + \int_a \int_b \frac{\tilde{\rho}_a(\vec{r}) \tilde{\rho}_b(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' - \int_a \int_b \frac{\rho_a(\vec{r}) \rho_b(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}', \end{aligned}$$

and it is similar for δG^0 . To first order in δn_a and Δn_b this gives

$$\begin{aligned} \delta \Delta G + \delta \Delta E_{NN} &= \left[G[\tilde{n}_a] - G[n_a] + \int_a \int_b \frac{\rho_b^0(\vec{r}')}{|\vec{r} - \vec{r}'|} \delta n_a(\vec{r}) d\vec{r} d\vec{r}' \right] \\ &\quad - \left[G[\tilde{n}_a^0] - G[n_a^0] + \int_a \int_b \frac{\rho_b^0(\vec{r}')}{|\vec{r} - \vec{r}'|} \delta n_a^0(\vec{r}) d\vec{r} d\vec{r}' \right] \\ &\quad + \left[G[\tilde{n}_b] - G[\tilde{n}_b^0] + \int_b \int_a \frac{\rho_a(\vec{r}')}{|\vec{r} - \vec{r}'|} \Delta \tilde{n}_b(\vec{r}) d\vec{r} d\vec{r}' \right] \\ &\quad - \left[G[n_b] - G[n_b^0] + \int_b \int_a \frac{\rho_a(\vec{r}')}{|\vec{r} - \vec{r}'|} \Delta n_b(\vec{r}) d\vec{r} d\vec{r}' \right] \\ &\quad + \int_a \int_b \frac{\Delta \rho_a(\vec{r}) \delta \rho_b^0(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'. \end{aligned} \quad (2.12)$$

Now, from Eqs. (2.4) and (2.11) we can write

$$v_a(\vec{r}) = \frac{\delta G[n_a]}{\delta n_a(\vec{r})} + \int_b \frac{\rho_b(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}', \quad v_b(\vec{r}) = \frac{\delta G[n_b]}{\delta n_b(\vec{r})} + \int_a \frac{\rho_a(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'. \quad (2.13)$$

This means that if the external potential from region a is the same in B and \tilde{B} , Eq. (2.12) can be written as follows:

$$\begin{aligned} \delta \Delta G + \delta \Delta E_{NN} &= \int_a v_a(\vec{r}) \delta n_a(\vec{r}) d\vec{r} - \int_a v_a^0(\vec{r}) \delta n_a^0(\vec{r}) d\vec{r} + \int_b \tilde{v}_b^0(\vec{r}) \Delta \tilde{n}_b(\vec{r}) d\vec{r} \\ &\quad - \int_b v_b^0(\vec{r}) \Delta n_b(\vec{r}) d\vec{r} + \int_a \int_b \frac{\Delta \rho_a(\vec{r}) \delta \rho_b^0(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'. \end{aligned} \quad (2.14)$$

If the external potential from region a is different in B and \bar{B} , as for instance when the effective medium is jellium (where the positive background extends over all space), a term

$$\delta\Delta G_{\text{ext}} = \int_a \delta v_a^{\text{ext}}(\vec{r}) \Delta\rho_a(\vec{r}) d\vec{r} \quad (2.15)$$

must be included.

Adding Eqs. (2.15), (2.14), and (2.10) we get

$$\begin{aligned} \Delta\tilde{E} = \Delta E + \int_a \int_b \frac{\Delta\rho_a(\vec{r})\delta\rho_b^0(\vec{r}')}{|\vec{r}-\vec{r}'|} \\ + \int_a \delta v_a^{\text{ext}}(\vec{r}) \Delta\rho_a(\vec{r}) d\vec{r} + \delta\Delta \left[\sum \epsilon_i \right]. \end{aligned} \quad (2.16)$$

The approach adopted here is very similar in spirit to Andersen's proof¹¹ of the force formula used in calculating the electronic pressure in bulk materials. Also, the form of the result is similar. The force is also given by a purely electrostatic term and the change in the sum of the one-electron energies. Equation (2.16) can be considered as a generalization of the force formula to situations where the atoms are not just translated a small amount but moved to a completely new environment.

The simplest effective medium is a homogeneous electron gas. This leaves an ambiguity with regard to the choice of the electron-gas density. Here the guideline must be to make a choice as close to the real host as possible, that is, to make the correction terms in Eq. (2.16) small and to put as much as possible into the zeroth-order term ΔE . By analogy to the simple version of the theory reviewed in the Introduction, the effective-medium density can be chosen as the average of the real host density $n_0(\vec{r})$ over the atom-induced electrostatic potential $\Delta\phi_a$ in region a :

$$\bar{n}_0 = \frac{\int_a n_0(\vec{r}) \Delta\phi_a(\vec{r}) d\vec{r}}{\int_a \Delta\phi_a(\vec{r}) d\vec{r}}. \quad (2.17)$$

With this choice of \bar{n}_0 we have

$$\int_a \int_a \frac{n_0(\vec{r}) - \bar{n}_0}{|\vec{r}-\vec{r}'|} \Delta\rho_a(\vec{r}') d\vec{r} d\vec{r}' = 0.$$

This term can then be added to the right-hand side of Eq. (2.16) to give

$$\Delta\tilde{E} = \Delta E + \int_a \phi_0(\vec{r}) \Delta\rho_a(\vec{r}) d\vec{r} + \delta\Delta \left[\sum \epsilon_i \right]. \quad (2.18)$$

Here

$$\phi_0(\vec{r}) = \int d\vec{r}' \frac{\rho_0(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

is the host electrostatic potential, and it has been

used so that ϕ_0 is zero in the effective medium. The particular choice of \bar{n}_0 , Eq. (2.17), thus replaces the unscreened external potential in Eq. (2.15) by the screened host potential. By analogy to the simple version of the theory, this averaging procedure also has the property that the result, Eq. (2.18), is equivalent to a gradient expansion of the embedding energy in the limit of slow-density variations.⁶

It is seen that, written in the form of Eq. (2.18), the new version of the theory looks very much like Eqs. (1.1) and (1.4) except for the fact that the electrostatic energy integral is restricted to the region close to the atom, and except for the extra term $\delta\Delta(\sum \epsilon_i)$. This term describes the effects of the region outside the close vicinity of the atom on the embedding energy. If there are strong scattering centers (large phase shifts) in this region, the one-electron energies will change considerably. If, on the hand, there are no such strong scatterers, as for instance on a jellium surface, this term will be small and the simple version of the theory should be applicable. The term $\delta\Delta(\sum \epsilon_i) = \Delta E^{\text{cov}}$ describes the covalent aspects of the binding since it will be governed mainly by the possibility of finding a resonance between the atomic- and host-derived one-electron levels.

The result, Eq. (2.18), is exact to first order in δn_a and δn_b , though usually, approximations must be introduced in order to evaluate it. The zeroth-order term $\Delta E = \Delta E^{\text{hom}}(\bar{n}_0)$ and the electrostatic correction are easily calculated as in the simple version of the theory. In evaluating the electrostatic integral it is usually assumed that the atom is neutral inside region a . This is consistent with the assumption, Eq. (2.9), that the atom-induced potential is zero outside a . In practice this means renormalizing Δn slightly. The electrostatic term can then be simplified even further, since the second term in Eq. (2.16) is zero and the third term can be written

$$\int_a \int_a \frac{\bar{n}_0}{|\vec{r}-\vec{r}'|} \Delta\rho_a(\vec{r}') = -\alpha_{\text{at}} \bar{n}_0. \quad (2.19)$$

The total embedding energy is then

$$\Delta\tilde{E} = \Delta E^{\text{hom}}(\bar{n}_0) - \alpha_{\text{at}} \bar{n}_0 + \Delta E^{\text{cov}}. \quad (2.20)$$

The treatment of the covalent term is more difficult. In principle, it requires a calculation of the one-electron spectrum for the atom in the real host, that is, for the low-symmetry system. The procedure is simplified by the fact that only one calculation is needed since $\delta\Delta(\sum \epsilon_i)$ must be calculated for *fixed potentials* and not the self-

consistent ones. The real advantage of the scheme is, however, that in many cases the bulk of the interaction energy is provided by the other two terms in Eq. (2.20). In such cases ΔE^{cov} can be treated more approximately than the rest. This does not mean that the term is not important in, e.g., explaining the (small) differences between different geometries, but just that a larger relative error can be accepted on a small-correction term. In the next section a number of such examples will be treated.

III. APPLICATIONS

A. Helium

The covalent term is simplest for the rare gases where it is basically zero. This is because the rare-gas core levels are so far away in energy from any of the host levels that there is only a very small covalent interaction. Another simplification for the rare gases is the (almost) linearity of ΔE^{hom} with n_0 (Fig. 1). If we write $\Delta E^{\text{hom}}(n_0) = \alpha n_0$ then Eq. (2.20) takes the particularly simple form

$$\Delta E(\vec{r}) = \alpha_{\text{eff}} \bar{n}_0(\vec{r}), \quad (3.1)$$

where $\alpha_{\text{eff}} = \alpha - \alpha_{\text{at}}$ with α_{at} defined in Eq. (2.19). For He, $\alpha = 275 \text{ eV } a_0^3$ (Ref. 12) (at metallic densities) in the local density approximation. Choosing a radius $R_{\text{cut}} = 2.5a_0$ of region a , we find that $\alpha_{\text{at}} = 126 \text{ eV } a_0^3$ at all densities and thereby $\alpha_{\text{eff}} = 149 \text{ eV } a_0^3$. The scheme has been applied to calculations of helium trapping energies in bulk-metal vacancies¹³ and to the calculation of the repulsive part of the helium-surface scattering potential.^{14,15} In the latter case the simplicity of the form, Eq. (3.1), is particularly valuable when the scattering potential, determined experimentally by helium diffraction, is to be transferred into information about the surface electronic and geometrical structure.

The reliability of the simple theory in the case of helium-trapping energies in vacancies is illustrated in Fig. 2. In Fig. 3 the insensitivity of the calculated energies with respect to variations in R_{cut} is shown. The results are seen to depend on R_{cut} only when region a becomes too small to contain the atom or when it overlaps too much with the host cores.

B. Hydrogen in transition metals

As an example, where the covalent term cannot be neglected we shall treat hydrogen as an intersti-

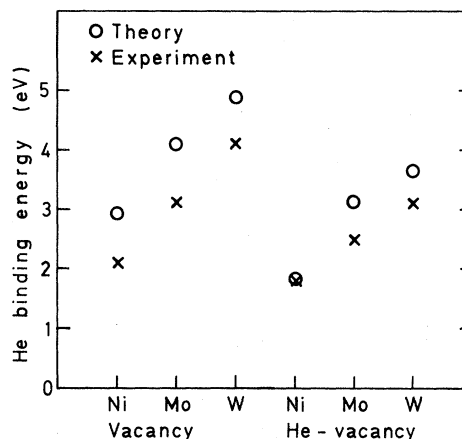


FIG. 2. Calculated vacancy-trapping energies (interstitial binding energy minus binding energy in a vacancy) for helium in the metals where experimental numbers exist for comparison (Ref. 26). Both trapping in an empty vacancy and in a vacancy preoccupied with one helium atom are considered. The input host densities \bar{n}_0 stem from overlapping atomic densities (from Ref. 13).

tial impurity in the metals from K to Cu. The hydrogen 1s level will interact strongly with the valence bands of these hosts. Often, all or most of the binding of hydrogen to the transition metals is ascribed to such a hybridization, in particular with the d bands.¹⁶ In the present approach, the covalent term ΔE^{cov} measures the difference in the hybridization of the hydrogen level when going from the homogeneous effective medium to the transition-metal host. We first note that even in the transition metals the s and p phase shifts are rather free-electron-like. This means that the difference between the s , p -1s hybridization in the

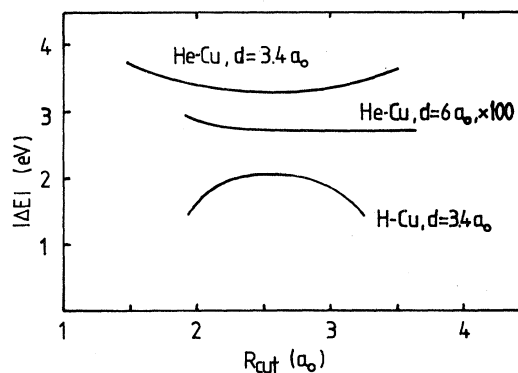


FIG. 3. Dependence of the calculated embedding energies on the radius R_{cut} of region a for interstitial He in Cu, He outside Cu surface at typical He energy in diffraction experiment, and interstitial H in Cu.

homogeneous electron gas and the real host is small. We thus only consider the effects of the host d electrons.

When hydrogen is embedded in a homogeneous electron gas, the $1s$ level is shifted down just below the bottom of the band and doubly occupied for all electron-gas densities in the metallic range.¹⁷ When the potential inside the atomic sphere v_a is shifted rigidly into the $3d$ host the common-energy zero is the "local bottom of the band" or the local value of the host effective potential. This ensures the smoothest transition between v_a and \tilde{v}_b . The $1s$ - d interaction is thus between a $3d$ band around the Fermi level ϵ_F , and a hydrogen-derived level situated around the effective potential V^0 in the interstitial region.¹⁸ In Fig. 4 this is shown schematically. The hydrogen level is pushed down (bonding) whereas the d levels are pushed up (antibonding). Because ϵ_F and V^0 are always well separated in energy we can treat the d - $1s$ hybridization in perturbation theory. To second order in the $1s$ - d hopping integral V_{ad} , the covalent term is

$$\Delta E^{\text{cov}} = \int_a [n_0(\vec{r}) - \bar{n}_0] \Delta V_a(\vec{r}) d\vec{r} + \left[\sum_{d \text{ occ}} \frac{|V_{ad}|^2}{\epsilon_d - \epsilon_a} - \sum_d \frac{|V_{ad}|^2}{\epsilon_d - \epsilon_a} \right]. \quad (3.2)$$

Here the first term giving the first-order contribution includes all the host electrons, not just the d electrons. The first-order term involving the overlap of the atomic electrons with the potential outside region a has been neglected, as discussed in

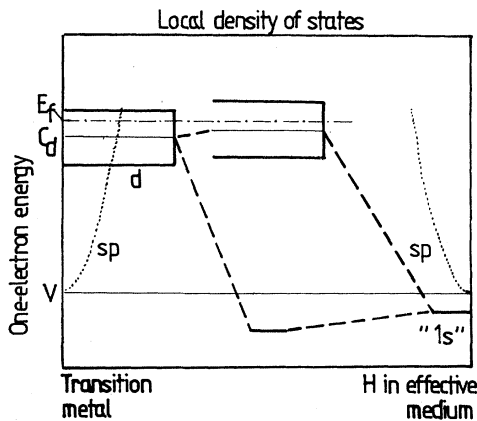


FIG. 4. Schematic picture of the hydrogen $1s$ —metal $3d$ hybridization in the effective-medium theory. The picture is basically that of two levels (the d bond and the $1s$ level) interacting to form bonding and antibonding levels. The interaction with the s - p electrons, on the other hand, is basically the same in the effective medium and in the real solid.

the beginning of this paragraph. The first term can be evaluated directly from a knowledge of the host density $n_0(\vec{r})$ and the hydrogen-induced potential Δv_a in a homogeneous electron gas. By comparing the first term to Eq. (2.17) it is seen that this term must scale roughly with the average density \bar{n}_0 . It is found that a proportionality constant of $-\alpha_v = -31 \text{ eV } a_0^3$ describes the term well for all densities except the lowest (K and Ca), where the absolute size of the error is very small. The next two terms represent antibonding and bonding contributions to the d - $1s$ hybridization in the real host.

Equation (3.2) can be simplified by noting that $\epsilon_d - \epsilon_a$ is much larger than the d -band width so that $\epsilon_d - \epsilon_a \simeq C_d - \epsilon_a \simeq C_d - V^0$, where C_d is the center of the d band and V^0 is the value of the metal effective potential at the hydrogen site. We further assume V_{ad} to be independent of ϵ_d . Equation (3.2) can then be written

$$\Delta E^{\text{cov}} = -\alpha_v \bar{n}_0 - 2(1-f) \frac{|V_{ad}|^2}{C_d - V^0}, \quad (3.3)$$

where f is the degree of filling of the part of the d bands with the right symmetry, to give a nonzero V_{ad} , and the factor of 2 comes from summing over spin (magnetic effects are neglected). The hopping integral is conveniently estimated in the atomic sphere approximation (ASA) formalism of Andersen *et al.*¹⁹ In the ASA, the potential is assumed spherically symmetric around each atom. The orbitals (here metal $3d$ and hydrogen $1s$) are approximated by muffin-tin orbitals decaying like an inverse power of distance from the atom. This makes the hopping integrals very simple. For the s - d interaction considered here we have

$$|V_{ad}|^2 = \Delta_a \Delta_d \sum_{\vec{R}} \frac{1}{R^6}, \quad (3.4)$$

where Δ_a and Δ_d are functions of the potential and atomic radii of the individual atomic spheres only, and where \vec{R} runs over all lattice sites (the hydrogen atom is at the origin). Note that in the ASA the assumption of an energy independent V_{ad} is justified.

Combining all of this, the total hydrogen binding energy can be written in the following closed form:

$$\begin{aligned} \Delta E &= \Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0) + \Delta E^{\text{hyb}}, \\ \Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0) &= \Delta E^{\text{hom}}(\bar{n}_0) - \alpha_{\text{tot}} \bar{n}_0, \\ \Delta E^{\text{hyb}} &= -2(1-f) \frac{\Delta_d \Delta_a}{C_d - V^0} \sum_{\vec{R}} \frac{1}{R^6}. \end{aligned} \quad (3.5)$$

In Eq. (3.5) the properties of the host and the atom (hydrogen) are completely separated. The properties of the atom enter through the function $\Delta E_{\text{eff}}^{\text{hom}}$, the atom-induced electrostatic potential needed to

evaluate \bar{n}_0 , and the potential parameter Δ_d . By including a number of different calculations of ΔE^{hom} (see Ref. 17 for a collection) the following parametrized form for $\Delta E_{\text{eff}}^{\text{hom}}$ has been obtained:

$$\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0) = \begin{cases} 130n_0 \ln \left[\frac{\bar{n}_0}{0.004} \right] - 252\bar{n}_0 - 1.12 \text{ (eV)}, & 0.002 \leq \bar{n}_0 \leq 0.0127 \\ 398(\bar{n}_0 - 0.0127)^2 + 31\bar{n}_0 - 2.81 \text{ (eV)}, & 0.0127 \leq \bar{n}_0. \end{cases} \quad (3.6)$$

The average, Eq. (2.17), is calculated using the $\Delta\phi$ of hydrogen in an electron gas, but the result is basically independent of the electron-gas density. Even the free-atom potential can be used. A radius R_{cut} of $2.5a_0$ has been used for the atomic sphere in calculating \bar{n}_0 and α_{tot} . The insensitivity of the final result to this choice is illustrated in Fig. 3. As for helium, a fairly constant region is found around $R_{\text{cut}} = 2.5a_0$. The potential function Δ_d should have been evaluated for H in an electron gas. Since this value was not available, and the potential close to the proton is found to depend only slightly on the surroundings, the Δ_d evaluated for solid hydrogen has been used. One finds²⁰

$$\Delta_d = (15.24 - 2.99R_{\text{WS}})R_{\text{cut}}^{-1}$$

in units of eV for $1.5a_0 \leq R_{\text{WS}} \leq 4a_0$. Here R_{WS} is the metal Wigner-Seitz radius and $R_{\text{cut}} (= 2.5a_0)$ is the hydrogen-sphere radius.

The properties of the host metal enter Eq. (3.5) through the electron density $n_0(\vec{r})$, the effective potential V^0 at the hydrogen site, and the parameters Δ_d , f , and C_d characterizing the d band. The electron density used is simply a superposition of atomic charge densities.²¹ This has been shown to give an error of less than 10% in the open sites

considered here.¹³ V^0 is calculated from $n_0(\vec{r})$ and therefore also has the superposition form. The band-structure parameters have been taken from Andersen and Glötzel.²⁰ Only the nearest neighbors are included in the sum, Eq. (3.4). The input parameters and the individual terms in the calculation of the hydrogen heats of solution are shown in Table I.

In Fig. 5 the total binding energy of interstitial hydrogen in the metals from K to Cu is shown together with the experimental low-concentration heats of solution.²² A remarkable agreement is seen in the trends along the series. In the figure the two contributions $\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0)$ and ΔE^{hyb} are also shown. It is seen how the major part of the total binding energy and most of the trends stem from the terms depending only on \bar{n}_0 . For most of the metals \bar{n}_0 is such that $\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0)$ is linear in \bar{n}_0 (Fig. 1). The variations thus directly reflect the variations in the interstitial electron density. These variations can be fully understood on the basis of the cohesive properties of the bulk metals.^{1(b)} For Ca and K, \bar{n}_0 is so low, however, that $\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0)$ bends over and starts increasing again with decreasing \bar{n}_0 .

Apart from the dip around Mn, which is con-

TABLE I. Crystal structure, hydrogen site of lowest energy, Wigner-Seitz radius R_{WS} , center of the d band relative to the effective potential in the interstitial region $C_d - V^0$, hopping integral entering Eq. (3.4), relative filling of the d -band f , averaged interstitial electron density \bar{n}_0 [Eq. (2.17)], and the different components of the hydrogen binding energy ΔE [Eq. (3.5)] for the metals from K to Cu.

	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
	bcc	fcc	hex	hex	bcc	bcc	fcc	bcc	hex	fcc	fcc
	tetr.	oct.	oct.	oct.	tetr.	tetr.	oct.	tetr.	oct.	oct.	oct.
$R_{\text{WS}} (a_0)$	4.862	4.122	3.427	3.052	2.818	2.684	2.699	2.662	2.621	2.602	2.669
$C_d - V^0$ (eV)	8.1	6.5	9.9	11.6	14.2	13.6	9.9	10.9	10.4	8.3	
$\Delta_d \Delta_s$ (eV ²)	201.0	252.9	200.8	156.0	123.9	99.7	85.33	72.2	62.8	54.9	
f	0.00	0.05	0.15	0.25	0.36	0.45	0.55	0.65	0.75	0.85	1
$\bar{n}_0 (a_0^{-3})$	0.002	0.005	0.010	0.017	0.028	0.033	0.024	0.031	0.032	0.026	0.021
$\Delta E_{\text{eff}}^{\text{hom}}$ (eV)	-1.95	-2.25	-2.45	-2.25	-1.80	-1.62	-2.00	-1.70	-1.66	-1.96	-2.11
ΔE^{hyb} (eV)	-0.14	-0.41	-0.68	-0.83	-0.86	-0.83	-0.54	-0.50	-0.32	-0.18	0
ΔE (eV)	-2.10	-2.66	-3.33	-3.08	-2.72	-2.45	-2.54	-2.20	-1.98	-2.14	-2.11

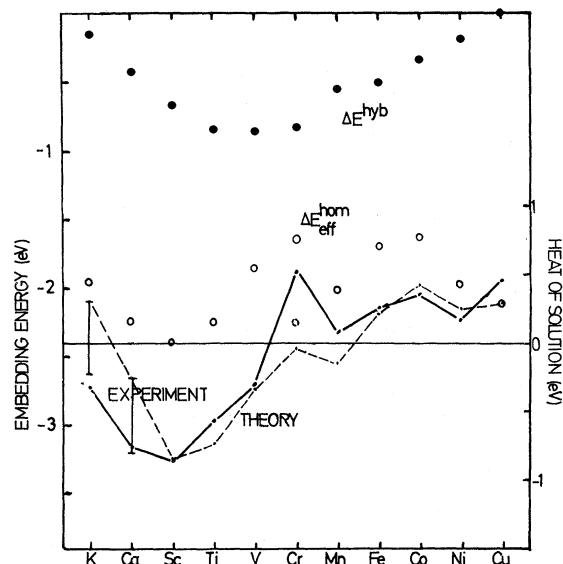


FIG. 5. Comparison of the calculated hydrogen binding energies to the experimentally determined heats of solution (Ref. 22) for the metals from K to Cu. The heat of solution is the embedding energy minus the binding energy in the H_2 molecule (-2.4 eV per atom). Also shown are the individual contributions in Eq. (3.5), $\Delta E_{\text{eff}}^{\text{hom}}$ (open circles), and ΔE^{hyb} (filled circles). For K and Ca, ΔE is also shown for a complex where the metal-H bond length has been allowed to relax. The real value is expected to lie in between these two extremes indicated by error bars (see text). The dashed circle for Cr denotes ΔE for nonmagnetic Cr.

nected with the magnetism in the $3d$ series,^{1(b)} the same variation in \bar{n}_0 , and thereby in ΔE , is expected for the $4d$ and $5d$ series in accordance with experiment.²² The variation of the hydrogen heat of solution perpendicular to the rows is illustrated in Fig. 6 for Ni, Pd, and Pt. The anomalous tendency of Pd to absorb hydrogen is clearly seen to be a consequence primarily of the open Pd lattice (\bar{n}_0 is low).

The variation of the hybridization term is rather smooth. To the right in the series, it is determined by the $(1-f)$ term in Eq. (3.5) which simply comes from the fact that the fewer d electrons there are in the band, the fewer antibonding electrons there will be after the $1s-3d$ hybridization has been taken into account. Left of V, the large values of R_{WS} lead to a weaker and weaker hybridization ($|V_{ad}|^2$ decreases).

The hybridization term is most important in explaining the difference between Cu and Ni (although the theory does not describe this too well). In Cu, ΔE^{hyb} is zero since both the bonding and the antibonding levels are occupied. This is not

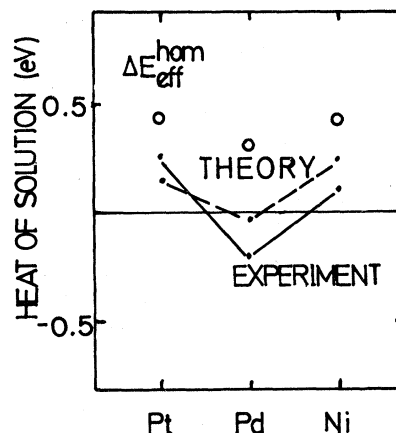


FIG. 6. Comparison of experimental and theoretical heat of solution for H in Ni, Pd, and Pt. The $\Delta E_{\text{eff}}^{\text{hom}}$ contribution is also shown. The experimental values are the hydride heats of formation (Ref. 27). Experimental heats of solution only exist for Ni (0.18 eV) (Ref. 22) and for Pd (-0.1 eV) (Ref. 22).

true for Ni, and even though \bar{n}_0 is larger for Ni than for Cu, hydrogen is bound strongest in Ni. Finally, it is interesting to note that the general shape of the hybridization-energy curve in Fig. 5 is very similar to that calculated by Muscat²³ in his embedded-cluster method for chemisorption energies.

Neither relaxation of the nearest-neighboring metal atoms nor the zero-point motion of the hydrogen atom has been included. For the open sites considered here both effects should be small (~ 0.1 eV) and of opposite sign. The effect of relaxations is small because the metal-metal bonds (as measured by, e.g., the cohesive energy) are usually much stronger than the H-metal bond. This is not true to the far left in the series (in particular for K and Ca). Here relaxing the nearest neighbors towards the hydrogen will increase the binding considerably.

In Fig. 5 the two extremes where the metal-H bond length is determined by the pure-metal lattice or by the metal-hydrogen interaction (neglecting the metal-metal interactions) are shown as an error bar for K and Ca. The true answer will lie somewhere in between. The too-small binding found in K and Ca may also be due to an underestimate of Δ_a . For these metals R_{WS} is actually outside the limits of validity for the formula used for Δ_a . The other noticeable difference between theory and experiment is for Cr. Here the discrepancy may be related to the fact that the magnetic state of Cr is very easily destroyed.²⁴ Even small concentrations

of hydrogen might thus lead to nonmagnetic Cr. With the use of the (calculated²⁴) $R_{WS} = 2.62a_0$ of paramagnetic Cr, which is lower than the value of Table I, the charge density \bar{n}_0 increases and a better agreement is found (see dashed circle in Fig. 5). In general it seems that in cases where the H-metal distance is small (e.g., Cr) or where the metal core is large (e.g., Pt) the interaction is not quite repulsive enough. This is probably related to the neglect of the s - p pseudopotential, or equivalently, to the fact that the orthogonalization to the metal cores is not completely included through the $\Delta E^{\text{hom}}(\bar{n}_0)$ term.

IV. CONCLUSIONS

The new effective-medium result, Eq. (2.20), has been seen to be able to reproduce both the absolute magnitudes as well as the trends for the binding of helium and hydrogen impurities in a large number of metals. This gives some confidence in the method as a way of estimating binding energies. The expression Eq. (2.20) also provides a way of splitting the interaction energy up into its different components. The first term represents the kinetic energy repulsion and the energy gain when the valence shell of the atom is filled. The second term is purely electrostatic and the third represents the covalent interaction. For helium impurities the first term dominates due to the kinetic energy part of it. For hydrogen impurities the first term also dominates, but here it is the tendency of hydrogen to form a (heavily screened) negative ion that is most important. In the present formulation the covalent term only expresses the difference in hybridization between the real host and the effective medium. For the transition metals the effective medium mainly describes the influence of the free-electron-like s - p electrons on the impurity. Roughly speaking, the interaction with the d band (through the covalent term) is thus considered *after* the interaction with the s - p bands has been taken into account. That is why ΔE^{cov} is so relatively unimportant. This provides a way of looking at, e.g., H-metal bonds, which is complementary to the method usually adopted, where the interaction with the d band is considered first, and the s - p electrons afterwards (if they are considered at all).²⁵ Which way of looking at the bond is most profitable must depend on the system in question. If the two first terms in Eq. (2.20) are dominating, as for H and He, then the present approach has

many advantages, as discussed in Secs. II and III. If, on the other hand, $\Delta E^{\text{hom}}(n_0)$ gives only a small part of the binding, then perhaps another approach will be better. This will mainly be the case for the one electropositive elements where the tendency to form a negative ion is not large enough to provide a considerable part of the binding (cf. Fig. 1).

When a diatomic molecule is considered, it is of course, in principle, the same whichever of the two atoms is regarded as embedded in the other. In practice, it will always be easiest to pick the most electronegative atom as the one to embed in the other, since the first term in Eq. (2.20) will then be largest. This also means that the method is not very suited for homonuclear molecules.

With the above limitations in mind, the method should easily be applicable to a large number of systems. The immediate extensions include the impurity problem with impurities other than He and H and the chemisorption problem. It should also be kept in mind that the effective medium can, in principle, be any system and not just a homogeneous electron gas. The guideline in choosing the effective medium must be (1) that it resembles the real host as much as possible in the vicinity of the embedded atom and (2) that the embedding problem is tractable for this system. The embedding scheme used by Muscat and News⁵ to calculate chemisorption energies can thus be thought of as an effective-medium approach with a jellium *surface* as the effective medium. When small energy differences are considered it is most likely that the two first terms in Eq. (2.18) do not change appreciably so that the whole energy difference will be given by the change in the one-electron energies. This may be one way of explaining why a large number of qualitative conclusions in chemistry can be reached on the basis of an understanding of the changes in the one-electron spectrum, and why only the one-electron energy change has to be considered in, e.g., explaining the trends and absolute magnitudes in the transition-metal alloy heats of formation.^{2,3}

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