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Corrections to the effective-medium theory of embedding energies: Interstitial hydrogen in metals

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A scheme for approximating the embedding energy ΔE of atoms in inhomogeneous host systems is proposed. A perturbation expansion for the correction to the uniform effective-medium approximation for ΔE is developed, and the lowest-order correction is shown to be both a good approximation and efficiently calculable within a density-functional theory. Numerical tests of the method using the Thomas–Fermi–von Weiszacker kinetic energy functional are presented. These tests involve the embedding of H at a vacancy in jellium, at tetrahedral and octahedral sites in Li and in K through Cu, and along the octahedral to tetrahedral path in Cu. The calculated results for H in Li and Cu are in good agreement with corresponding results from cluster calculations.

I. INTRODUCTION

The embedding energy ΔE of an impurity atom in a host solid is defined as the total energy of the combined system less the energies of the isolated host and impurity atom. An approximate but *efficient* method of calculating ΔE for an impurity embedded in an arbitrary host system would be very useful. For example; a computer simulation of the diffusion of an interstitial impurity in a host metal repeatedly requires the impurity energy, which gives the host-impurity forces, as a function of environment within the host. This same quantity is needed to investigate lattice relaxation about the impurity,[1-5] for studies of impurity-defect interactions,[6-16] and for the calculation of quantum states of impurities in solids.[14,17,18]

There are two general approaches to the calculation of ΔE. One is the cluster calculation, in which the host plus the impurity is represented by a small cluster of atoms, and the total energy of the cluster is calculated with and without the impurity. Examples of this approach for H in metallic hosts are the calculations of Shillady *et al.*[19] for Li_9H and $Li_{11}H$ clusters, of Cremaschi and Whitten[15] for a $Ti_{43}H$ cluster, and of Guo and Ellis[16] for $Cu_{14}H$, $Cu_{13}H$, and $Cu_{13}NiH$. This type of calculation is, however, so computer-time consuming that it is not very practical, at least at present, for investigation lattice relaxation around the impurity, and totally impractical for more complex simulation studies of atom motions.

In the second approach, an effective medium, in which the embedding energy $\Delta\bar{E}$ of the impurity is known, is constructed in a way which is intended to satisfactorily mimic the local region within the host where the impurity is to be embedded. Then, ΔE for the impurity in the real host is that for the impurity in the effective medium, $\Delta\bar{E}$, plus correction terms which are taken to be small. The most popular choice of effective medium is uniform jellium of a suitable density $\bar{n}$. Several calculations exist for the embedding energy $\Delta\bar{E}(\bar{n})$ of H in uniform jellium both via Kohn-Sham (KS) calculations[6,20-25] and by alternative many-body methods.[26] These ideas based on the electron density also form the basis of an empirical scheme for constructing interatomic energies. Daw and Baskes[13] introduced an ansatz for the total energy, with several parameters fitted to bulk properties. In addition to a repulsive pairwise interaction the ansatz contains a term accounting for the energy of the atom in the host material in terms of the local host electron density. The scheme has met with considered success in treating defect and other properties of metallic systems, but a first-principles understanding of the scheme is awaited.

When the effective medium approximation $\Delta E \approx \Delta\bar{E}$ is used with uniform jellium as the effective medium, the approximation has been called the uniform density approximation (UDA). A number of attempts have been made to develop corrections to the UDA which would account for the inhomogeneous nature of real host environments. Popovic and Stott[6] formulated corrections to $\Delta\bar{E}$ which were first order in the metal pseudopotential. Norskov and Lang[24] used a sampled host density plus a first-order electrostatic correction to calculate the chemisorption energy of H near a jellium surface. Stott and Zaremba[23] also suggested a sampled host density, and in addition developed a gradient expansion in the host electron density. They found[23] good agreement with exact KS calculations of the binding energies of H and He to jellium vacancies.

These prescriptions for the correction terms, designed for slowly varying or nearly uniform host densities, were not successful for H in the interior of real host metals.[27,28] In these more inhomogeneous hosts, the electrostatic potentials are so large and rapidly varying that these approximation schemes fail. Because of this, two other methods of evaluating corrections to $\Delta\bar{E}$ have been proposed. Norskov's formulation[29] has been successful in a wide variety of applications,[10,18,29,30] although its theoretical basis remains to some extent ambiguous. Three of the present authors proposed[28] a scheme in which the rearrangement energy ΔE_R defined by[23]

$$\Delta E = \Delta E_R + Z[\mu - \phi^0(\mathbf{R})] , \tag{1}$$

where Z is the charge on the impurity nucleus, μ is the host chemical potential, and $\phi^0(\mathbf{R})$ the host electrostatic potential[31] at the impurity position **R**, is regarded as the fundamental quantity of interest. This scheme, with ΔE_R approximated by its UDA value, gives good results for the embedding energy of H in a number of transition metals.[28]

The rearrangement energy is the focus on the present work as well. We investigate the extent to which formulating corrections to the UDA value of the rearrangement energy, $\Delta\bar{E}_R$, is a more reliable procedure than the formulation of corrections to the UDA embedding energy. One obvious advantage is that other calculational techniques well suited to pure host systems (e.g., band structure) can be used to obtain accurate values for the host property $\mu-\phi^0(\mathbf{R})$, while perhaps more approximate treatments are suitable for ΔE_R.

In this work, a perturbation expansion for the correction to $\Delta\bar{E}_R$ is developed. The expansion is in terms of the small change in external potential needed to alter the screening electron density Δn around the impurity embedded in the real host to $\Delta\bar{n}$, the jellium screening density. Using the variational principle of Hohenberg and Kohn,[32] we then show that the lowest-order perturbation theory correction can be expressed as a variational bound involving $\Delta\bar{n}$ in place of Δn. This procedure is useful in practical calculations, where $\Delta\bar{n}$ is known while Δn is (often) not. Numerical tests are presented which demonstrate that the lowest-order correction is a good approximation to the full correction.

In order to test this approach, numerical calculations have been performed for H in a variety of hosts using the Thomas-Fermi-von Weiszacker kinetic energy functional and the local-density approximation for exchange and correlation. Results are presented for H in a jellium vacancy corresponding to Al, the differences in ΔE_R and ΔE between the tetrahedral (T) and octahedral (O) sites in Li and in K through Cu, and along the octahedral→tetrahedral jump path in Cu. The lowest-order perturbation correction to $\Delta\bar{E}_R$ agrees well with the exact results in these cases. The calculated values of ΔE_R^{T-O} and ΔE^{T-O} (tetrahedral minus octahedral values) for H in Li and Cu are also compared with corresponding results from cluster calculations and are in good agreement with them. A comparison of the model results for ΔE_R with deduced experimental values for H in K through Cu is also made.

II. DENSITY-FUNCTIONAL THEORY OF THE EMBEDDING ENERGY

Our work is in the context of density-functional theory, and so we begin by reviewing the expression of the embedding and rearrangement energies within this formalism. We consider only systems consisting of electrons in external potentials $v_{\text{ext}}(\mathbf{r})$ generated by positive charge distributions $n_+(\mathbf{r})$ which satisfy Poisson's equation

$$\nabla^2 v_{\text{ext}}(\mathbf{r})=4\pi n_+(\mathbf{r}) \; . \tag{2}$$

The electronic energy functional for such a system can be written as[32]

$$E_{v_{\text{ext}}}[n]=G[n]+\tfrac{1}{2}\int d^3r\, n(\mathbf{r})v_{\text{el}}(\mathbf{r})+\int d^3r\, n(\mathbf{r})v_{\text{ext}}(\mathbf{r}) \; , \tag{3}$$

where

$$G[n]=T_s[n]+E_{\text{xc}}[n] \tag{4}$$

is the sum of the independent particle kinetic (T_s) and exchange-correlation (E_{xc}) energy functionals, and

$$v_{\text{el}}(\mathbf{r}_1)=\int d^3r_2 n(\mathbf{r}_2)/r_{12} \tag{5}$$

is the electrostatic potential due to the electrons. The Hohenberg-Kohn variational principle states that $E_{v_{\text{ext}}}[n]$ is minimized by the ground-state electron density.

The specific systems considered here are characterized by a host external potential $v^0_{\text{ext}}(\mathbf{r})$ and the corresponding positive charge density $n^0_+(\mathbf{r})$ and host ground-state electron density $n^0(\mathbf{r})$ (i.e., host quantities have the superscript 0), and by the impurity external potential $\Delta v_{\text{ext}}(\mathbf{r})$ with corresponding positive charge density $\Delta n_+(\mathbf{r})$. The free-atom density for the impurity is denoted $n_a(\mathbf{r})$, and the free-atom energy is E_a. All systems are to be charge neutral.

The combined system of host plus impurity thus has an external potential

$$v_{\text{ext}}(\mathbf{r})=v^0_{\text{ext}}(\mathbf{r})+\Delta v_{\text{ext}}(\mathbf{r}) \tag{6}$$

and electron density

$$n(\mathbf{r})=n^0(\mathbf{r})+\Delta n(\mathbf{r}) \; , \tag{7}$$

where $\Delta n(\mathbf{r})$ is the screening density around the impurity. The embedding energy of the impurity in the host is

$$\Delta E=E_{v_{\text{ext}}}[n]-E_{v^0_{\text{ext}}}[n^0]-E_a-\int d^3r\, n^0_+(\mathbf{r})\Delta v_{\text{ext}}(\mathbf{r}) \tag{8}$$

including, as the last term, the change in self-interaction energy of the positive charge distribution. The rearrangement energy is related to ΔE by (1), with

$$\phi^0(\mathbf{r})=v^0_{\text{el}}(\mathbf{r})+v^0_{\text{ext}}(\mathbf{r}) \; . \tag{9}$$

The three contributions to ΔE in (1) may be pictured physically as corresponding to the three step process in (i) adding the impurity positive charge to the frozen host $[-Z\phi^0(\mathbf{R})]$, (ii) adding the Z electrons at the chemical potential ($+Z\mu$), and (iii) then allowing the electrons to rearrange to form the minimum energy screening cloud (ΔE_R).

III. CORRECTIONS TO ΔE_R FOR INHOMOGENEOUS HOSTS

The decomposition (1) of ΔE into ΔE_R plus the property $\mu-\phi^0$ of the undisturbed host permits the use of independent sources for the two quantities. At least for perfectly periodic solids, $\mu-\phi^0$ is now accurately known from band-structure calculations, and, if $\mu-\phi^0$ is known, finding suitable approximations to ΔE_R may be an easier task than finding suitable approximations to ΔE. Some evidence that this is so is contained in Ref. 28, although we postpone summarizing that evidence until Sec. IV. The approximation used in Ref. 28 to evaluate the embedding of H at position $\mathbf{R}$ within a transition-metal host was the UDA, $\Delta E_R \approx \Delta \bar{E}_R(n^0(\mathbf{R}))$, where $\Delta \bar{E}_R(\bar{n})$ is the rearrangement energy of H in a uniform host[28] of density $\bar{n}$. In this section we formulate the correction

$$\delta\Delta E_R = \Delta E_R - \Delta \bar{E}_R \tag{10}$$

to this approximation for nonuniform hosts. The same leading-order correction can be expressed either through perturbation theory or variationally. The perturbation theory is physically more transparent, while the variational expression is much easier to evaluate in practice.

A. Perturbation theory correction to $\Delta \bar{E}_R$

The rearrangement energy can be concisely written as[26]

$$\Delta E_R = \int_0^1 d\lambda \int d^3r\, \Delta n^\lambda(\mathbf{r}) \frac{\partial}{\partial \lambda} \Delta v^\lambda_{\rm ext}(\mathbf{r}) , \tag{11}$$

which involves an integration of a coupling constant λ. In this expression, $\Delta v^\lambda_{\rm ext}$ is an external potential which vanishes for $\lambda=0$ and increases with increasing λ to become the full impurity external potential at $\lambda=1$, and Δn^λ is the corresponding ground-state screening density. It is useful to consider three different systems in which an impurity, with its external potential varying in this way with a coupling constant $0 \le \lambda \le 1$, is to be embedded in a host. These systems are (Fig. 1): (i) The real system, for which we write ΔE_R, $n^\lambda = n^0 + \Delta n^\lambda$, $v^\lambda_{\rm ext} = v^0_{\rm ext} + \Delta v^\lambda_{\rm ext}$, etc. (ii) The reference system, in which the corresponding quantities $\Delta \bar{E}_R$, $\bar{n}^\lambda = \bar{n}^0 + \Delta \bar{n}^\lambda$, $\bar{v}^\lambda_{\rm ext} = \bar{v}^0_{\rm ext} + \Delta \bar{v}^\lambda_{\rm ext}$, etc., are denoted by a bar above. This system is chosen so that $\bar{n}^0 = n^0(\mathbf{R})$ and $\Delta \bar{v}^\lambda_{\rm ext} = \Delta v^\lambda_{\rm ext}$. (iii) An intermediate system, in which the corresponding quantities $\Delta \tilde{E}_R$, $\tilde{n}^\lambda = \tilde{n}^0 + \Delta \tilde{n}^\lambda$, $\tilde{v}^\lambda_{\rm ext} = \tilde{v}^0_{\rm ext} + \Delta \tilde{v}^\lambda_{\rm ext}$, etc., are denoted by a tilde above. This system is chosen so that $\tilde{v}^0_{\rm ext} = v^0_{\rm ext}$ and so $\tilde{n}^0 = n^0$, but $\Delta \tilde{n} = \Delta \bar{n}$. Thus, real host properties are used along with the jellium screening density to construct the intermediate system. Note that $\Delta \tilde{v}^\lambda_{\rm ext}$ is *not* the potential due to a point nucleus. In particular, the difference

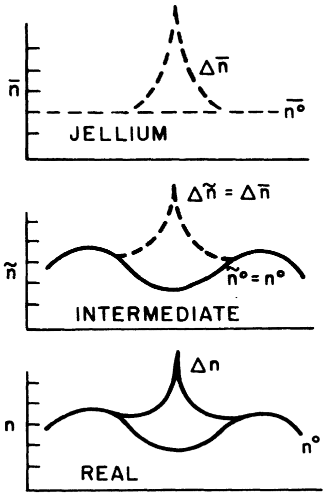

FIG. 1. Schematic representation of the electron densities of the three systems involved in the perturbation theory correction to $\Delta \bar{E}_R$.

$$w^\lambda_{\rm ext} = \Delta \tilde{v}^\lambda_{\rm ext} - \Delta v^\lambda_{\rm ext} \tag{12}$$

is the potential required to support the artificial intermediate system.

The intermediate system is introduced because it is believed[25] that the screening density in the real system looks very much like that in a suitably chosen reference (see, e.g., Fig. 2). When this is so, $w^\lambda_{\rm ext}$ will be a small perturbation. By construction, and using (11),

$$\Delta \tilde{E}_R = \Delta \bar{E}_R + \int_0^1 d\lambda \int d^3r\, \Delta \tilde{n}^\lambda(\mathbf{r}) \frac{\partial}{\partial \lambda} w^\lambda_{\rm ext}(\mathbf{r}) , \tag{13}$$

which can be interpreted as the change on going from the reference system to the intermediate system. To find $\delta\Delta E_R$, however, we still need the change on going from the intermediate system to the real system.

This latter change requires switching off the additional potential $w^1_{\rm ext}$ which was imposed to hold the screening cloud at its jellium shape in the presence of the true host potential. We now cancel $w^1_{\rm ext}$ by switching on the further potential $-\lambda' w^1_{\rm ext}$. This, again from (11), yields

$$\Delta E_R = \Delta \tilde{E}_R - \int_0^1 d\lambda' \int d^3r\, \Delta \tilde{n}^{1,\lambda'}(\mathbf{r}) w^1_{\rm ext}(\mathbf{r}) \tag{14}$$

since the rearrangement energy steps are additive. The symbol $\Delta \tilde{n}^{1,\lambda'}$ denotes the screening cloud along the path from the intermediate system to the real system, where λ was set to 1 (the intermediate system) and then λ' increased from zero. This screening cloud is, however, not easily determined. Nevertheless, if we write

$$\Delta \tilde{n}^{1,\lambda'} = \Delta \tilde{n}^1 + \delta\Delta \tilde{n}^{1,\lambda'} , \tag{15}$$

then the last term of

$$\Delta E_R = \Delta \tilde{E}_R - \int d^3r\, \Delta \tilde{n}^1(\mathbf{r}) w^1_{\rm ext}(\mathbf{r}) - \int_0^1 d\lambda' \int d^3r\, \delta\Delta \tilde{n}^{1,\lambda'}(\mathbf{r}) w^1_{\rm ext}(\mathbf{r}) , \tag{16}$$

which we shall call $\delta\Delta E_R^{(2)}$, is second (and higher) order in the assumed small perturbation $w_{\rm ext}$, since $\delta\Delta \tilde{n}^{1,\lambda'}$ is already first order. Thus, neglecting the last term $\delta\Delta E_R^{(2)}$ of (16) and using (13),

$$\delta\Delta E_R \approx \delta\Delta E_R^{(1)} = -\int_0^1 d\lambda \int d^3r\, w^\lambda_{\rm ext}(\mathbf{r}) \frac{\partial \Delta \tilde{n}^\lambda(\mathbf{r})}{\partial \lambda} \tag{17}$$

to lowest order in $w^\lambda_{\rm ext}$.

In order to evaluate (17), $w^\lambda_{\rm ext}$ must be found. This can be done by inverting the Euler equation for the intermediate system. Minimization of $E[n]$ with the total number of electrons fixed, yields the Euler equation

$$\frac{\delta}{\delta n(\mathbf{r})}(E-\mu N)=0\ . \tag{18}$$

Explicitly using the expression (3) for $E[n]$ yields

$$\mu_T(\mathbf{r})+\mu_{\rm xc}(\mathbf{r})+v_{\rm el}(\mathbf{r})+v_{\rm ext}(\mathbf{r})-\mu=0\ , \tag{19}$$

with

$$\mu_T(\mathbf{r})=\frac{\delta T}{\delta n(\mathbf{r})} \tag{20}$$

and

$$\mu_{\rm xc}(\mathbf{r})=\frac{\delta E_{\rm xc}}{\delta n(\mathbf{r})}\ . \tag{21}$$

If the kinetic and exchange-correlation energy functionals, and the density, are known, μ_T and $\mu_{\rm xc}$ can be evaluated. The density is known for the intermediate system with the impurity present and the Euler equation yields

$$\Delta\tilde{v}^{\lambda}_{\rm ext}=\tilde{\mu}-\tilde{\mu}_T-\tilde{\mu}_{\rm xc}-\tilde{v}^{0}_{\rm el}-\Delta\tilde{v}^{\lambda}_{\rm el}-\tilde{v}^{0}_{\rm ext}\ . \tag{22}$$

Since $\tilde{\mu}$, $\tilde{v}^{0}_{\rm el}$, and $\tilde{v}^{0}_{\rm ext}$ are the same as in the real host system, while $\Delta\tilde{v}^{\lambda}_{\rm el}$ is the same as in the reference, $w^{\lambda}_{\rm ext}$ can be found.

This perturbation theory derivation of the correction (17) makes the criterion for its validity apparent. It is a good approximation when the reference screening cloud $\Delta\tilde{n}^{\lambda}$ is similar to that in the real host metal Δn^{λ}. Some numerical tests are presented in Sec. V. To evaluate (17), however, it is necessary to find $w^{\lambda}_{\rm ext}$ and $\Delta\tilde{n}^{\lambda}$ for a number of values of λ. This can be circumvented by a variational method which we now describe.

B. Variational calculation of $\delta\Delta E_R^{(1)}$

Equation (8) defines the embedding energy ΔE. More generally, we can invoke the Hohenberg-Kohn variational principle to define an *embedding energy functional* as follows. Let n^0 be the ground-state density of the host, as before. Let, however, $n=n^0+\Delta n$ be any density which keeps the host plus impurity system charge neutral. Then

$$\Delta E[\Delta n,n^0]=E_{v_{\rm ext}}[n^0+\Delta n]-E_{v^0_{\rm ext}}[n^0]-E_a-\int d^3r\, n^0_+(\mathbf{r})\Delta v_{\rm ext}(r) \tag{23}$$

can be regarded as a functional of Δn, which we call the embedding energy functional. Minimization of $\Delta E[\Delta n,n^0]$ with respect to variations of the screening density Δn gives the embedding energy ΔE. Furthermore, substitution of any Δn in the embedding energy functional gives a variational upper bound to ΔE, and hence, through (1) if $\mu-\phi^0(\mathbf{R})$ is known, a corresponding bound to the rearrangement energy. If the reference screening density $\Delta\bar{n}$ is close to the true screening density Δn, this suggests the variational estimate

$$\Delta E_R^{\rm var}=\Delta E[\Delta\bar{n},n^0]-Z[\mu-\phi^0(\mathbf{R})]=\Delta\bar{E}_R+\delta\Delta E_R^{(1)}\ . \tag{24}$$

As shown in the Appendix, this variational estimate of ΔE_R gives a correction $\delta\Delta E_R$ precisely equal to the first-order correction $\delta\Delta E_R^{(1)}$ that was obtained in (17). By inverting the Euler equation (19) for the host, the difference between the chemical and electrostatic potentials in (24) can be eliminated with the result

$$\delta\Delta E_R^{(1)}=\Delta E[\Delta\bar{n},n^0]-Z\frac{\delta G[n^0]}{\delta n^0(\mathbf{R})}-\Delta\bar{E}_R\ . \tag{25}$$

Thus, if the host density n^0, jellium screening density $\Delta\bar{n}$, and kinetic-exchange-correlation functional G are known, the lowest-order correction $\delta\Delta E_R^{(1)}$ to the (known) jellium rearrangement energy can be evaluated. This expression for $\delta\Delta E_R^{(1)}$ involves neither a coupling constant integration nor the explicit evaluation of the intermediate system perturbing potential $w_{\rm ext}$, and is the one which we use in the calculations to follow.

IV. A MODEL QUANTUM MECHANICS AND A MODEL SOLID

There is some evidence supporting the view that finding suitable corrections to $\Delta\bar{E}_R$ for inhomogeneous hosts may be an easier task than finding the corresponding corrections to $\Delta\bar{E}$. An investigation[28] of the embedding energy of H in metallic hosts using the UDA rearrangement energy—in which ΔE_R is approximated by its value $\Delta\bar{E}_R$ for jellium at the local density $n^0(\mathbf{R})$—showed that one part of the heat of solution of H in transition metals was attributable to the host property $\mu-\phi^0(\mathbf{R})$. A second part of the systematic trend was reflected in the jellium rearrangement energy. The procedure produced good, even quantitative, agreement to the left of the 3*d* and 4*d* transition-metal rows, but the jellium approximation seemed to be ~1 eV too low to the right of the rows, e.g., in Co, Ni, and Cu. These discrepancies were attributed to the corrections required to the UDA rearrangement energies because of the large inhomogeneities in the electron density in these hosts. We are now in a position to examine this hypothesis. We do so by applying our formal expressions for the correction $\delta\Delta E_R$ within an approximate and fully local-density-functional theory in which $G[n]$ is explicitly known. Our aim is to develop a means of estimating the required 10% correction[33] to the UDA values that seems to be required for these metals.

Our numerical calculations serve a second purpose as well. It is to test how well our lowest-order correction $\delta\Delta E_R^{(1)}$, which is easy to calculate, approximates the full correction $\delta\Delta E_R$ in reasonably realistic metallic environment. To test this, we must be able to carry out the full calculation as well as evaluating the lowest-order correction.

To numerically test our correction to the jellium rearrangement energy we introduce both a model quantum mechanics and a model solid. This allows us to calculate the rearrangement energy correction for H exactly and to compare our lowest-order approximation with this result. We believe that our model solid provides a reasonably realistic representation of a transition metal host, and that the model quantum mechanics is sufficiently accurate to serve as a test of the perturbation expansion.

The model quantum mechanics that we use is Thomas–Fermi–Dirac–von Weizsacker theory with correlation added (TFDWC) as described by Plumer and Stott.[34] This is a local-density-functional theory in which $G[n]$ is explicitly known. The kinetic energy functional is

$$T[n]=T_0[n]+T_W[n]\ , \tag{26}$$

where

$$T_0[n]=\tfrac{3}{10}\int d^3r\, n(\mathbf{r})[3\pi^2 n(\mathbf{r})]^{2/3} \tag{27}$$

is the Thomas-Fermi kinetic energy and

$$T_W[n]=\frac{\lambda_W}{8}\int d^3r\frac{[\nabla n(\mathbf{r})]^2}{n(\mathbf{r})} \tag{28}$$

is the additional von Weizsacker term. The von Weizsacker coefficient is chosen to be $\lambda_W=0.56$ throughout this work, for that is the value which satisfactorily reproduces[34] the "hydrogen energy curve" (which is the embedding energy of H in jellium as a function of the jellium density). The exchange-correlation energy functional used is that of Gunnarson and Lundqvist,[35] without spin polarization.

The model of the host used here is a "spherical solid" model. The host-metal electron density has been constructed by superposing Hartree-Fock atomic densities[36] using the solid-state electronic configurations tabulated by Norskov.[29] This host density is then spherically averaged about the site $\mathbf{R}$ at which the proton is to be placed. This spherically averaged density is then used as n^0, and in principle the host external potential v^0_{ext} required to generate this density within the TFDWC model is obtained by inverting the host TFDWC Euler equation. In practice only the total host electrostatic potential (9) is required, and is given by

$$\phi^0(r)-\mu=-\frac{\delta G[n^0]}{\delta n^0(\mathbf{r})}\ . \tag{29}$$

This is then used, with $\mu=\mu_0$, in the TFDWC Euler equation for the host plus impurity to determine Δn, whereas the jellium screening density, $\Delta\bar{n}$, is given by setting $\phi^0(\mathbf{r})=0$. The rearrangement energy is then determined by

$$\begin{aligned}\Delta E_R[\Delta n,n^0]= {} & G[n^0+\Delta n]-G[n^0]\\ & -\int d^3r\frac{\delta G[n^0]}{\delta n^0(\mathbf{r})}\Delta n(\mathbf{r})\\ & +\tfrac{1}{2}\int\int d^3r_1d^3r_2\frac{\Delta n(\mathbf{r}_1)\Delta n(r_2)}{r_{12}}\\ & +\int d^3r\,\Delta v_{\text{ext}}(\mathbf{r})\Delta n(\mathbf{r})-E_a\ .\end{aligned} \tag{30}$$

Note that the second and third terms resemble a perturbation expansion of the first in the quantity $\Delta n/n^0$ which is expected to be small away from the impurity nucleus (see Fig. 2). The approximations used in this work are for $G[n]$ and $n^0(\mathbf{r})$. The lowest-order perturbation theory correction $\delta\Delta E_R^{(1)}$ which we are testing, can be found by replacing Δn by $\Delta\bar{n}$ in (30), and subtracting $\Delta\bar{E}_R$ from the result.

V. NUMERICAL RESULTS

In order to test the variety of approximation schemes developed in the previous sections, the results of numerical calculations using expression (30) for ΔE_R are presented here and compared with other theories and experimental results. The numerical procedure for solving the TFDWC Euler equation for a given spherical host density $n^0(|\mathbf{r}-\mathbf{R}|)$ and hydrogen impurity, was the same as used by Plumer and Stott[34] except that here we solved for the screening density Δn or $\Delta\bar{n}$ instead of the full electron density n. Solutions for the jellium screening density $\Delta\bar{n}$ required only about 10 sec of IBM 3081 CPU time, while solutions for the real screening density Δn took up to 10 CPU minutes.

In some cases it will be more convenient to compare values of the embedding energy instead of values of ΔE_R. For these cases, the most realistic value of $\phi^0(\mathbf{R})-\mu$ will be used, and this is generally not the TFDWC reconstructed value. Thus, in this section our "calculated embedding energy" ΔE refers to

$$\Delta E=[\Delta E_R]_{\text{TFDWC}}+Z[\mu-\phi^0(\mathbf{R})]_{\text{other source}}\ . \tag{31}$$

Since $[\Delta\bar{E}_R]_{\text{TFDWC}}$ reproduces[34] the hydrogen energy curve of Kohn-Sham (KS) theory, this in effect means that our TFDWC quantum mechanics plus our spherical-solid model is only used for the correction $\delta\Delta E_R$ when ΔE is calculated.

A. H in a vacancy in jellium

As a simple test system, we have studied H at the center of a charge 3 vacancy in jellium of $r_s=2.07$, which corresponds to the mean conduction electron density of Al metal. For comparison, full KS calculations were carried out using the Gunnarson-Lundqvist exchange-correlation potential[35] (i.e., the same as in the TFDWC calculations), and we shall regard these KS calculations as the "exact" results. This system is spherically symmetric, so the spherical-solid model averaging described in Sec. IV is not involved. Since for a uniform system the TFDWC theory used gives a good description of the KS hydrogen energy curve,[34] the system of H in a jellium vacancy provides two tests: (i) A full TFDWC calculation investigates how well the TFDWC energy functional reproduces the KS rearrangement and embedding energies in an inhomogeneous host. (ii) Comparison of the full and lowest-order corrected TFDWC calculations of the rearrangement energy indicates the accuracy of the lowest-order correction $\delta\Delta E_R^{(1)}$ (17) or (25) to the rearrangement energy.

It should be noted that the jellium vacancy is not a very inhomogeneous host in comparison with real metals. The electron density variation for the jellium vacancy is about a factor of 5, with the density at the center being 0.0044 a.u. in comparison with the background density of 0.0269 a.u. This is an appreciably smaller variation, and involves rather lower densities, than in, e.g., a transition-metal host.

The results of both the TFDWC and KS calculations are summarized in Table I. The KS values of the host

TABLE I. Rearrangement energy for H in a charge 3 vacancy in jellium of $r_s=2.07$. All energies are in eV. The proton is located at $\mathbf{R}=\mathbf{0}$, the center of the vacancy. The quantities tabulated are the rearrangement energies ΔE_R, the corresponding jellium values $\Delta\bar{E}_R$ at the local density $n^0=0.0044$ a.u., the lowest-order correction $\delta\Delta E_R^{(1)}$, the higher-order correction $\delta\Delta E_R^{(2)}$, the difference between the local host electrostatic and chemical potentials, and the embedding energy from (31).

	TFDWC	KS
ΔE_R	2.00	2.03
$\Delta\bar{E}_R$	0.80	0.40
$\delta\Delta E_R^{(1)}$	1.32	
$\Delta\bar{E}_R+\delta\Delta E_R^{(1)}$	2.12	
$\delta\Delta E_R^{(2)}$	-0.12	
$\phi^0(0)-\mu$	7.10	3.94
ΔE	-1.94	-1.91

density $n^0(\mathbf{r})$ were used in the TFDWC calculation, and the TFDWC value quoted for ΔE uses the KS value for $\mu-\phi^0(0)$ in (31). TFDWC reproduces the KS rearrangement energy very well. The lowest-order approximation $\Delta\bar{E}+\delta\Delta E_R^{(1)}$ reproduces ΔE_R to within ~ 0.1 eV. The TFDWC and KS values for $\mu-\phi^0(0)$ do not agree because of the difference in the true and TFDWC reconstructed host external potential v_{ext}^0. For this system, then, it appears that (i) our TFDWC model quantum mechanics satisfactorily reproduces the rearrangement energy (but not the host potential) and (ii) the lowest-order estimate of ΔE_R is good to about ± 0.1 eV, which is totally adequate for the approximate theories which it is our aim to develop.

B. H in Li

The embedding energy differences of H between various sites including the tetrahedral and octahedral sites within nine-atom and eleven-atom Li clusters have been calculated by Shillady *et al.*[19] using a Hartree-Fock molecular-orbital (HFMO) method. We shall compare our TFDWC calculation with their results, although our calculations are for a H atom in an infinite bcc Li lattice of lattice constant 3.49 Å. We found that all the density and potential contributions from our superposed host-metal atoms are sufficiently short-ranged that our TFDWC results are independent of sample sizes beyond a few neighbor shells, so in practice only the necessary couple of neighbor shells were used in constructing our spherical-solid model of the host-metal density. It should be noted, however, that the HFMO results are known[37] to be dependent on cluster size, at least for clusters of ≤ 16 atoms.

Only the embedding energy differences were reported by Shillady *et al.*,[19] and it would be necessary to know the host electrostatic potential ϕ^0 to obtain the difference in the rearrangement energies between two sites. (The difference does not require μ, although a value for μ would be required to find the rearrangement energy at a site.) Consequently, we compare only the embedding energies.

Our TFDWC spherical model results are compared with the HFMO results of Shillady *et al.*[19] for the tetrahedral and octahedral sites in Table II. Because of the uncertainties above, and because of the differing treatments of exchange and correlation in the two calculations, the comparison is not as direct as for the vacancy in jellium of the preceding section. The comparison does, however, test the spherical-solid aspect of our model as well as the TFDWC aspect. The host electrostatic potential $\phi^0(\mathbf{R})$ used to convert our TFDWC rearrangement energies to embedding energies via (31) was obtained by superposing the host-metal atom electrostatic potentials. The embedding energy difference [using the superposition value for the difference in $\phi^0(\mathbf{R})-\mu$ which is 0.12 eV] is in, perhaps, fortuitously good agreement between the two calculations, but suggests that our model is a reasonable one, at least for light-metal hosts. The comparison of $\Delta\bar{E}_R+\delta\Delta E_R^{(1)}$ for the two sites also indicates that the lowest-order correction $\delta\Delta E_R^{(1)}$ is adequate.

C. H in Cu

Guo and Ellis[16] have reported a Hartree-Fock-Slater (HFS) (i.e., a local exchange-correlation potential) calculation of the differences in embedding energy of H between various sites within a 14-atom Cu cluster. They also report the self-consistent host electrostatic potential ϕ^0, so that the differences in rearrangement energy can be obtained.

Table III gives the comparison of our TFDWC results with those of Guo and Ellis.[16] The host electrostatic potential $\phi^0(\mathbf{R})$ is again obtained by superposing the host-metal atom electrostatic potentials. Again, the lowest-order corrected value $\Delta\bar{E}_R+\delta E_R^{(1)}$ gives a good estimate of ΔE_R, although the discrepancy $\delta E_R^{(2)}$ is larger than in the previous examples, perhaps because of the larger potential and density variations in Cu. Although the tetrahedral-octahedral embedding energy change compares well with that of Guo and Ellis (using the superposition value for the difference $\phi^0-\mu$ which is ~ 1.2 eV), both the rearrangement energy and electrostatic potential differences show a discrepancy of ~ 1 eV and differ in sign. The reconstructed TFDWC host potential

TABLE II. Rearrangement energies for H at the tetrahedral (T) and octahedral (O) sites in Li metal. The symbol T-O indicates the difference of the tetrahedral-site value from the octahedral-site value, and $\mathbf{R}$ denotes the position of the proton. The remaining notation is that of Table I.

		TFDWC		HFMO[a]
Site	T	O	T-O	T-O
ΔE_R	0.71	0.83	-0.12	
$\Delta\bar{E}_R$	0.45	0.45		
$\delta\Delta E_R^{(1)}$	0.34	0.50		
$\Delta\bar{E}_R+\delta\Delta E_R^{(1)}$	0.79	0.95	-0.16	
$\delta\Delta E_R^{(2)}$	-0.08	-0.12		
$\phi^0(\mathbf{R})-\mu$	1.90	1.56	0.34	
ΔE			-0.24	-0.24

[a] From Ref. 19.

TABLE III. Rearrangement energies for H at the tetrahedral and octahedral sites in Cu metal. The notation is that of Table II.

	TFDWC			HFS[a]
Site	T	O	T-O	T-O
ΔE_R	1.23	1.13	0.10	-0.7
$\Delta \bar{E}_R$	-0.32	-0.13	-0.19	
$\delta\Delta E_R^{(1)}$	1.90	1.49	0.41	
$\Delta \bar{E}_R + \delta\Delta E_R^{(1)}$	1.58	1.36	0.22	
$\delta\Delta E_R^{(2)}$	-0.35	-0.23	-0.12	
$\phi^0(R)-\mu$	7.7	3.6	$+4.1$	-1.9
ΔE			1.3	1.2

[a] Reference 16.

difference compares very poorly with the other two theoretical values here.

Figure 2 shows the TFDWC exact and jellium quasiatom densities as well as the spherical-solid model host density for Cu at the octahedral site. The difference between Δn and $\Delta \bar{n}$ is seen to be small, suggesting that the perturbation theory of Sec. III is appropriate. For $r \geq 2$ a.u., $\Delta n \ll n_0$ so that the integrands of the first three terms of expression (30) for ΔE_R sum to a small contribution in this region of the host. Thus, the rearrangement energy depends on only the properties of the host within a local region. The cusp appearing in Δn, but not $\Delta \bar{n}$, occurs at the H-Cu nearest-neighbor distance $r \approx 3.4$ a.u. Although the calculation of the change in screening of the Cu nuclei requires considerable computational effort, this detail contributes a negligible amount to ΔE_R. There are no Friedel oscillations[6] at large r, a result which is expected of a local kinetic energy functional.[32] Friedel oscillations also introduce computational difficulties[23] but contribute little to ΔE_R.

Figure 3 compares the embedding energies and the electrostatic potentials from the two calculations along a line joining the octahedral and tetrahedral sites (with all the curves constructed from six or seven points). There is a marked difference in the barrier height along the path, which is ~1 eV higher in the HFS cluster calculation. Comparison with the electrostatic potentials shows that this larger barrier in the HFS calculation corresponds to a change in sign of the rearrangement energy difference which is not reflected in our TFDWC calculations. A notable feature of these curves is the close agreement between the "exact" and perturbation approximation TFDWC results.

Also shown in Fig. 3 are the results of Norskov's effective medium theory[29] of the H embedding energy. The embedding energy variation along this path within the Cu host is smaller than given by our TFDWC calculation, and in poorer agreement with the HFS cluster results. These comparisons with cluster calculations should

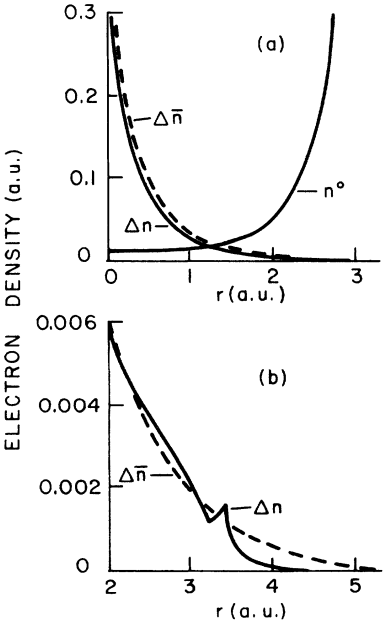

FIG. 2. Electron densities for H in Cu at the octahedral site showing the pure Cu density $n^0(r)$ from the spherical-solid model, the exact quasiatom density $\Delta n(r)$ and the UDA quasiatom density $\Delta \bar{n}(r)$ corresponding to jellium at density $n^0(0)$ from the TFDWC calculation. Note the vertical scale change between (a) and (b).

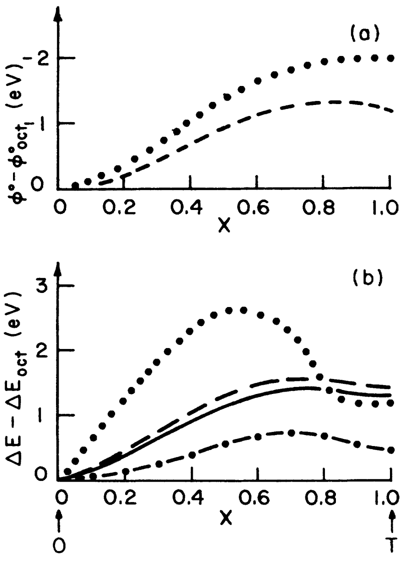

FIG. 3. The octahedral to tetrahedral jump path for H in Cu with x indicating the fractional distance to the tetrahedral site. (a) The pure Cu electrostatic potential relative to the octahedral site from the cluster calculation of Ref. 16 (dotted curve) and from the spherical-solid model (dashed curve). (b) The embedding energy relative to the octahedral site from the exact TFDWC calculation (solid curve), from the TFDWC calculation in the perturbation theory approximation (dashed curve), from the cluster calculation (dotted curve), and from the results of the Norskov theory (dash-dotted curve).

be viewed with some caution, however, because of the cluster size dependence reported by Rao *et al.*[37]

D. Heat of solution of H in the metals K through Cu

We now attempt to compare our results with experiment. The two are not directly comparable, for the H heat of solution contains contributions from lattice relaxation which give an energy lowering of perhaps a few tenths of an eV, and a zero-point energy increase of ≤ 0.1 eV. The other potentially relevant measured quantity is the activation energy for diffusion, ~ 0.5 eV, but this need not correspond to the barrier height of e.g., Fig. 3(a) because of the presence of thermal lattice vibrations in addition to lattice relaxation and zero-point energy effects. Consequently, we shall only compare our results with the experimental heat of solution.

Figure 4 shows the calculated rearrangement energies across the K to Cu row, and also the approximation $\Delta\bar{E}_R+\delta\Delta E_R^{(1)}$, which is within ≤ 0.1 eV of ΔE_R for all metals except Cu, where the discrepancy is 0.2 eV. Since the rearrangement energy is primarily governed by the near-neighbor arrangement, we have for simplicity replaced hcp or more complex structures (Mn) by fcc. The sites chosen were the octahedral site in the fcc structure and the tetrahedral site in the bcc structure. These were found to be the lowest-energy sites within our TFDWC theory.

For comparison, we also show "experimental" rearrangement energies in Fig. 4. These are taken from Ref. 31, where they were obtained as follows. The band-structure calculations of Moruzzi *et al.*[38] use the same crystal structure as used here, and give the difference between their average interstitial electrostatic potential and the chemical potential. This was used for $\phi^0(\mathbf{R})-\mu$, and the experimental heat of solution, plus the binding energy per atom of the H_2 molecule (2.25 eV) gives ΔE. The rearrangement energy was then obtained from Eq. (1).

The TFDWC spherical-solid correction $\delta\Delta E_R$ to $\Delta\bar{E}_R$ shows a slow monotonic increase from ~ 0.5 eV to ~ 1.0 eV across the row. This improves the agreement with experiment for Co, Ni, and Cu, but destroys the earlier[28] good agreement for the preceding members of the row. Although possibly a defect of the TFDWC spherical solid model, there is no apparent reason for a sudden onset of the correction at Co. Other possibilities are the muffin-tin potentials of Moruzzi *et al.*[38] do not provide sufficient detail in the interstitial region,[39] or that lattice relaxation and zero-point energy effects are more significant than the figures quoted above suggest.

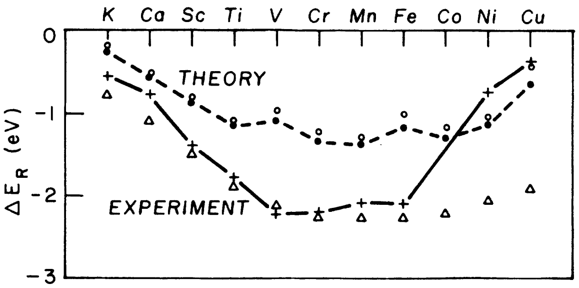

FIG. 4. The rearrangement energy including the TFDWC correction. The best theoretical values are $\Delta\bar{E}_R+\delta\Delta E_R$ (solid circles with dashed line) using $\Delta\bar{E}_R$ from Ref. 28 and the exact TFDWC $\delta\Delta E_R$. Also shown are $\Delta\bar{E}_R+\delta\Delta E_R^{(1)}$ (open circles) and $\Delta\bar{E}_R$ (triangles). "Experimental" values (crosses with solid line) are from Ref. 28.

As well as testing the Thomas–Fermi–von Weizsacker kinetic energy, the kinetic energy functional formulated in Ref. 34 (the TFDWγC model) was also used in some corresponding numerical tests. The values of ΔE_R using this model differed from the TFDWC results up to 1 eV. Although this represents a worsening of agreement with the exact results for the case of H in the Al jellium vacancy, the TFDWγC model produced values for $\delta\Delta E_R$ from 0.2 to 0.5 eV lower than the TFDWC results for H in the transition metals (Fig. 4). The agreement between this model and the corresponding experimental results is to within ~ 0.2–~ 0.7 eV.

VI. DISCUSSION

Our calculations indicate that the lowest-order correction $\delta\Delta E_R^{(1)}$ is an excellent approximation to the full correction $\delta\Delta E_R$ to the UDA rearrangement energy for nonuniform hosts. Using the spherical-solid model host densities which mimic the hydrogen sites in transition and noble metals, $\delta\Delta E_R^{(1)}$ is within $\sim 10\%$ of $\delta\Delta E_R$, corresponding to a discrepancy ~ 0.1 eV. Because of its variational nature, $\delta\Delta E_R^{(1)}$ is always more positive than $\delta\Delta E_R$. Our major conclusion is, then, that our lowest-order correction $\delta\Delta E_R^{(1)}$, given by (17) and equivalently by (25), is a good approximation to the correction to the UDA rearrangement energy for H in metallic hosts, i.e., $\Delta\bar{E}_R+\delta\Delta E_R^{(1)}$ is a good approximation to ΔE_R. Using the variational expression (25), this correction is easily calculable. This procedure does, however, require an energy functional, and the development of improved approximate kinetic energy functionals of the electron density would be useful.

The hypothesis that approximate corrections to the effective medium theory are best formulated in terms of the rearrangement energy, rather than the full embedding energy, also is supported by the numerical results. Use of the TFDWC rearrangement energy along with realistic values of the host potential $\phi^0(0)-\mu$ give embedding energy differences in reasonable agreement with the more complex cluster calculations. In contrast, embedding energies constructed solely from TFDWC by using the TFDWC value of $\phi^0(0)-\mu$ as well are in very poor agreement with the cluster results.

Furthermore, the calculated H embedding energies by the procedure used here are in very satisfactory agreement with the results of other more accurate, but also very much more complex and time consuming, theoretical calculations for H in the jellium vacancy and for the differences between tetrahedral and octahedral sites in the metal clusters. However, the comparison of our results for the absolute H embedding energies with the experimental data across the K–Cu row is not as good, although the discrepancies, $\sim 0.5-1.2$ eV, are small with respect to the total rearrangement energy of H, which is ~ 1 Ry.

A possible explanation for the fact that the results for the tetrahedral-octahedral energy differences are much better than the absolute embedding energies for H in transition metals [apart from the possibility that the muffin-tin potential used for $\phi^0(\mathbf{R})$ is inadequate] is that the Thomas–Fermi–von Weizsacker kinetic energy functional is unable to properly describe complex interactions between the impurity atom and the host metal which arise from shell structure and that these effects partially cancel when differences between impurity sites are considered. It is also noteworthy that the energy of the H atom using the TFDWC model, with $\lambda_W = 0.56$, is quite poor ($E_a = -11.2$ eV) but that the error introduced by this result cancels when energy differences between sites are taken. The discrepancy between our results and those from the corresponding cluster calculation for the H embedding energy difference along the tetrahedral-octahedral path in Cu, as shown in Fig. 3, may be due to the nonspherical effects not accounted for in our calculation and the finite-cluster size effects in the calculation of Ref. 16, which are expected to become increasingly important as the H is moved away from the relatively symmetrical and open tetrahedral and octahedral sites.

In conclusion the perturbation theory correction to the rearrangement energy of the effective medium approximation has been shown to be a useful procedure. Our results also suggest that although the TFDWC energy functional may be inadequate for some purposes, the use of this simple model to calculate H embedding energy differences in metallic hosts within the perturbation theory approximation provides reasonable and easily obtainable results. The procedure presented in this work may also be useful in the calculation of embedding energies of larger ($Z > 1$) impurity atoms.

ACKNOWLEDGMENT

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APPENDIX: PROOF OF THE EQUIVALENCE OF THE PERTURBATIONAL AND VARIATIONAL ESTIMATES OF $\delta\Delta E_R^{(1)}$

To show that the quantity $\delta\Delta E_R^{(1)}$ appearing in (24) is the same as (17), it is sufficient to show that

$$\Delta E[\Delta n, n^0] - \Delta E[\Delta\bar{n}, n^0] = \delta\Delta E_R^{(2)} . \tag{A1}$$

To show this, construct the embedding energy functional for the intermediate system, and observe that

$$\Delta\tilde{E}[\Delta\bar{n}, n^0] = \Delta E[\Delta\bar{n}, n^0] + \int d^3r\, w_{\text{ext}}(\mathbf{r})[n^0(\mathbf{r}) + \Delta\bar{n}(\mathbf{r}) - n_+^0(\mathbf{r})] \tag{A2}$$

and

$$\Delta E[\Delta n, n^0] - \Delta\tilde{E}[\Delta\bar{n}, n^0] = \Delta E_R - \Delta\tilde{E}_R - \int d^3r\, w_{\text{ext}}(\mathbf{r})[n^0(\mathbf{r}) - n_+^0(\mathbf{r})] . \tag{A3}$$

Substitution of (16) and (A2) in (A3) proves (A1).

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