PHYSICAL REVIEW B VOLUME 22, NUMBER 4 15 AUGUST 1980

# Quasiatoms: An approach to atoms in nonuniform electronic systems

M. J. Stott and E. Zaremba
*Department of Physics, Queen's University, Kingston, Canada K7L 3N6*

(Received 20 December 1979)

A method of estimating the energy of an impurity in a host electronic system using density-functional theory is presented. The impurity ion plus its electronic screening cloud is treated as a unit and is used to define a *quasiatom*. The energy of the quasiatom is a functional of the host electron density in which it is immersed. In the simplest approximation it is given by the energy of the impurity in a uniform electron gas having a density equal to that of the host at the position of the impurity nucleus. This uniform-density approximation (UDA) is tested for light atoms in a variety of model and realistic situations and is found to be successful in reproducing qualitative trends. By developing a perturbation expansion for a weakly inhomogeneous host the UDA is shown to be the leading term in a rigorous expansion of the quasiatom energy in gradients of the host electron density, and corrections to second order in gradients are determined. As an example, these corrections are used in the calculation of the binding energy of a helium atom to a vacancy and excellent agreement with exact results is achieved. The perturbation expansion also suggests an ansatz for the quasiatom energy in which the host electron density is sampled by the quasiatom electrostatic potential. Tests of this ansatz are equally successful.

## I. INTRODUCTION

This paper concerns the energy of an atom that is added to an arbitrary electronic host system, such as to the interior of a metal, a metal surface, or a molecule. Methods for treating these systems to varying degrees of accuracy are already available. However, not all methods are practical and the specific method chosen is generally dictated by the complexity of the host system being considered. For example, small molecules can be treated using configuration interaction methods[1] which represent perhaps the most fundamental approach to the many-electron problem. However, for extended systems such as solids, this approach is not feasible and alternative methods must be sought. For these systems, density-functional theory[2,3] offers an equally fundamental approach which, with the frequently used local density approximation (LDA), appears to provide a good account of electron exchange and correlation effects. Aside from the LDA the only limitation of this method is the successful solution of a single-particle Schrödinger equation from which the electronic density can be obtained. This limitation is steadily being eroded by advances in computational capability and even complex situations, such as an impurity in a metal[4] or at a metal surface,[5-7] can now be handled either directly or when represented by embedding schemes[8] or cluster calculations.[9] The time is close, when, with sufficient computational effort, reliable energies for atoms in complicated host systems will be obtainable. Our aim here is not to add to these direct attacks on the problem, but rather to develop a qualitative scheme that can be used to correlate the behavior of a given atom in diverse hosts and that can yield, with little effort, rough predictions for energies in complex situations of practical interest.

An interstitial impurity in a metal provides an illustrative example of the kind of situations of interest. Unless the excitation spectrum of the impurity is the object of study, much of the work involved in the direct approaches is redundant and in some cases counterproductive. For example, in determining the energy of the impurity, the internal electronic structure must be recalculated for each new impurity position. Both the valence electron states and core levels change but, as we shall see, it seems that these are not independent of one another but conspire together to give a total electron density and energy for the impurity that are rather close to those of the free atom. However, changes of the density or energy from the free atom do occur, and it is these differences as the impurity is taken from one host to another that interest us. The focus of our attention is the degree to which these changes in the impurity atom are determined by the local host environment. To the extent that they are, the atoms of a perfect crystal can themselves be thought of as impurities in a host which thus provides a unified view of atoms in solids. Of course, only selected electronic properties can be considered in this fashion since many are strongly influenced by long-range crystalline order (e.g., single-particle energies, transport, etc.).

The emphasis in our approach is on treating the whole atom—nucleus or ion and electron polarization cloud—as a single unit or "quasiatom." Since the unit is electrically neutral its energy will be unaffected by electric potentials due to charge distributions far from the atom, e.g., electric dipoles at the surface of a metal. By concentrating on the atom and the way it is modified by the host rather than the ion as in pseudopotential theory,[10] the cancellation of large energies that result when valence electrons are stripped from the ion in one situation and replaced in another is avoided.

We try to identify those parameters of the host system that affect the quasiatom. For small atoms at least, calculations indicate that the quasiatoms are compact objects with localized energy densities, and it seems that the dominant feature determining the energy is the local host density. We are therefore led to a local density approximation for the whole atom which we shall term the *uniform-density approximation* (UDA). The quasiatom energy as a function of local density can be calculated once and for all in great detail by treating the atom as an impurity in a uniform electron gas. These energy curves for different atoms are in a sense universal since the quasiatom energy is determined (qualitatively at least) by a single parameter of the host, the host electron density at the position of the impurity nucleus, although more accurate results will undoubtedly involve additional host parameters.

The UDA was suggested in an earlier paper[11] (referred to as I) and tested in some simple model situations. The same idea has also been used by Larsen and Nørskov[12] for treating the behavior of H in metal vacancies and by Nørskov and Lang[13] for studying chemisorption. Surface reactions have also been considered by Lundqvist *et al.*[7] from a similar viewpoint. In this paper we present more extensive tests of the UDA which demonstrate its utility in various physical situations. In addition we develop a general theory of the quasiatom energy which provides ways of transcending this lowest-order approximation; these corrections are also tested.

The outline of the paper is as follows. In Sec. II we consider the general definition of the quasiatom energy in terms of density-functional theory. A convenient separation of the total energy is made into a localized self-energy of the quasiatom and its electrostatic interaction with the unperturbed host system. This then motivates the UDA for the atom. The basic ingredient of the local approximation is the energy curve for the atom in a uniform gas as a function of mean electron density. The method for calculating these curves is described in Sec. III, and a theorem relating the slope of the energy curve to the average electrostatic potential of the quasiatom is proved. Section IV contains a discussion of the energy curves for several light impurities, (H, He, Li) and characteristic features of these curves are accounted for. The UDA is then tested by applying it to various model situations such as the binding of an impurity to a vacancy, the chemisorption of hydrogen on a metal surface, and small molecules. In Sec. V we return to the question of justifying the uniform-density approximation by investigating its relation to a perturbation expansion of the quasiatom energy for a host system in which the variations in electron density are small and slowly varying. This analysis suggests quantitative corrections to the UDA and these are explored. The final section discusses prospects of the model for further applications as well as extensions of the basic concepts.

## II. QUASIATOM ENERGY

Consider a host system in which the ground-state electron density is $n_0(\vec{r})$ and in which the external field acting on the electrons is due to a rigid positive charge distribution $n_0^+(\vec{r})$. The total ground-state energy of the host can be written as a functional of $n_0(\vec{r})$,

$$E_0 = G[n_0] - \int d\vec{r}_1 \int d\vec{r}_2 \frac{n_0(\vec{r}_1) n_0^+(\vec{r}_2)}{r_{12}} + \frac{1}{2}\int d\vec{r}_1 \int d\vec{r}_2 \frac{n_0(\vec{r}_1) n_0(\vec{r}_2)}{r_{12}} , \qquad (1)$$

where the first term in (1) is the kinetic, exchange, and correlation energy functional and the two remaining electrostatic terms are due to the external field and electron-electron interactions, respectively. It is convenient to extract the electrostatic term explicitly from the total energy functional in the manner above so that any long-range electrostatic interactions can be treated properly. The effects concealed in $G[n_0]$ are expected to be short-ranged.

Consider next the effect of adding an external positive charge distribution $\Delta n_Z^+(\vec{r})$ of total charge $Z$ to the host. To be specific, we shall think of the perturbation as representing an "impurity" which is located interstitially in a "crystal" at the origin of coordinates. For simplicity we neglect any lattice relaxation around the impurity. The total ground-state electron density $n_Z(\vec{r})$ for the new configuration can be expressed as

$$n_Z(\vec{r}) = n_0(\vec{r}) + \Delta n_Z(\vec{r}) , \qquad (2)$$

where $\Delta n_Z(\vec{r})$ is the impurity screening cloud. If $Z$ extra electrons are added along with the nucleus, $\Delta n_Z(\vec{r})$ will be localized in the vicinity of the impurity (otherwise, in the case of a metal, a surface contribution to $\Delta n_Z$ will occur). The neutral unit consisting of the nucleus and its screening cloud will be termed a quasiatom.

The total energy for this situation will now be

$$E_Z = G[n_Z] - \int d\vec{r}_1 \int d\vec{r}_2 \frac{n_Z(\vec{r}_1)[n_0^+(\vec{r}_2) + \Delta n_Z^+(\vec{r}_2)]}{r_{12}} + \tfrac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \frac{n_Z(\vec{r}_1) n_Z(\vec{r}_2)}{r_{12}} + \int d\vec{r}_1 \int d\vec{r}_2 \frac{n_0^+(\vec{r}_1)\Delta n_Z^+(\vec{r}_2)}{r_{12}} , \tag{3}$$

and the change in energy associated with inserting the impurity can be written as

$$\Delta E = \left( G[n_Z] - G[n_0] - \int d\vec{r}_1 \int d\vec{r}_2 \frac{\Delta n_Z(\vec{r}_1)\Delta n_Z^+(\vec{r}_2)}{r_{12}} + \tfrac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\Delta n_Z(\vec{r})\Delta n_Z(\vec{r}_2)}{r_{12}} \right) + \int d\vec{r}\, \phi_Z(\vec{r})[n_0(\vec{r}) - n_0^+(\vec{r})] , \tag{4}$$

where

$$\phi_Z(\vec{r}) = \int d\vec{r}_1 \frac{\Delta n_Z(\vec{r}_1) - \Delta n_Z^+(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} \tag{5}$$

is the electrostatic potential of the screened impurity.

The term in large parentheses in (4) can be regarded as the self-energy $\Delta E_{\text{self}}$ of the impurity atom and, following the discussion in I, it is reasonable to assume that this self-energy is associated with a localized energy density. It contains the kinetic, exchange, and correlation energy through $G[n_Z] - G[n_0]$, and the two electrostatic terms account for the interaction between the impurity charge and its screening cloud and the classical electrostatic energy of the screening cloud. It is evident from (4) that the self-energy can be determined once $\Delta n_Z(\vec{r})$ and $n_0(\vec{r})$ are specified. Clearly it will be different from the isolated impurity atom energy $E_a$, and this change should in some sense reflect the impurity's local host environment. This can be stated more formally by noting that $\Delta n_Z(\vec{r})$ is a functional of the potential $v_0(\vec{r})$ associated with the positive charge distribution of the host. But $v_0(\vec{r})$ is itself a unique functional of the host density $n_0(\vec{r})$ and so, for a given impurity, $\Delta n_Z(\vec{r})$ can be viewed as a unique functional of the host electron density distribution $\Delta n_Z[n_0]$. Thus $\Delta E$ is itself a functional of $n_0(\vec{r})$.

Great benefits could accrue from identifying the features of the host environment of the impurity that determine its screening cloud and the corresponding change in energy from the free atom, and the remainder of this paper is devoted to a first attempt at this problem. Our ultimate goal is to express quantitatively the modification of the impurity atom energy in terms of accessible host parameters. It is to be hoped that the host electron-density distribution in the vicinity of the impurity plays the dominant role here and that it will be unnecessary to have detailed knowledge of the internal electronic structure of either the impurity or host (such as the perturbed band structure).

The additional term in (4), $\Delta E_{\text{es}}$, takes explicit account of the electrostatic interaction between the impurity quasiatom and the host. Since both of these are electrically neutral the interaction is double screened. Because of this it should be considerably smaller in magnitude than the single-screened interactions that usually arise in expressions for the energy. For instance, the structure-dependent part of the energy $\Delta E$ calculated using pseudopotentials to second order in perturbation theory involves a pair potential with Fourier transform

$$\phi_{IH}(\vec{q}) = \frac{w_I(\vec{q})\, w_H(\vec{q})}{4\pi/q^2} \left( \frac{1}{\varepsilon(\vec{q})} - 1 \right) + Z_I Z_H \frac{4\pi}{q^2} , \tag{6}$$

where $w$, $Z$, and $\varepsilon$ are, respectively, the bare pseudopotential, the valence, and the dielectric function; the subscripts refer to the impurity ($I$) and host ($H$) atoms. To avoid double counting of the electron interactions, (6) is single screened. In contrast the impurity-host interaction that would appear in the final term of the partition (4) is

$$\psi_{IH}(\vec{q}) = \frac{w_I(\vec{q})\, w_H(\vec{q})}{4\pi/q^2} \left( \frac{1}{\varepsilon^2(\vec{q})} - 1 \right) + Z_I Z_H \frac{4\pi}{q^2} , \tag{7}$$

which at small $q$ differs from (6) by a factor $1/\varepsilon(\vec{q}) \sim q^2/(q^2 + q_{\text{TF}}^2)$, where $q_{\text{TF}}^{-1}$ is the Thomas-Fermi screening length. The second-order pseudopotential expression for $\Delta E$ is of course equivalent to (4) in the weak potential approximation, but the partitioning of the energy chosen here may prove more convenient in some applications.

In the jellium limit where the host positive charge is smeared out to form a uniform continuum the impurity-host electrostatic interaction vanishes and (4) becomes

$$\begin{aligned} \Delta E &= \overline{\Delta E}\,(\bar{n}) \\ &= G[n_Z] - G[\bar{n}] - \int d\vec{r}_1 \int d\vec{r}_2 \frac{\Delta n_Z(\vec{r}_1)\Delta n_Z^+(\vec{r}_2)}{r_{12}} \\ &\quad + \tfrac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\Delta n_Z(\vec{r}_1)\Delta n_Z(\vec{r}_2)}{r_{12}} , \end{aligned} \tag{8}$$

where $n_0 = \bar{n}$ is the mean electron density of the jellium. If the electron density in the host is slowly varying on the scale of the impurity quasiatom, then

$$\Delta E \simeq \overline{\Delta E}(n_0(0)) , \tag{9}$$

where $n_0(0)$ is the host electron density at the origin where the impurity resides. The *uniform-density approximation* (9) is the leading term in an expansion of (4) in gradients of the host electron density. It is a local density approximation for the whole quasiatom, ion plus valence electrons. In Sec. V the UDA will be investigated further and corrections to it suggested.

The energy zero of $\Delta E$ in (4) is such that the impurity energy with respect to the neutral free impurity atom is $\Delta E - E_a$. On inserting the impurity, $Z$ electrons as well as the impurity ion are added to the host so that the potential energy zero in the host is irrelevant and in particular surface dipoles have no effect.

## III. IMPURITIES IN JELLIUM

The central quantity entering the uniform density approximation is the energy of an impurity in a uniform electron gas (jellium) as a function of mean gas density. As shown by Kohn and Sham[3] (KS), a formal solution of this problem is straightforward within the density-functional theory. The interacting many-body system can be recast into a system of noninteracting particles moving in an effective external potential,

$$v_{\mathrm{eff}}(\vec{r}) = \phi_Z(\vec{r}) + \left.\frac{\delta E_{\mathrm{xc}}[n]}{\delta n}\right|_{n_Z(\vec{r})}, \tag{10}$$

where $\phi_Z$ is given by (5) and $E_{\mathrm{xc}}[n]$ is the exchange and correlation energy functional. The electron density is given in terms of the single-particle wave functions $\psi_i(\vec{r})$ by

$$n_Z(\vec{r}) = \sum_{\varepsilon_i < \mu} |\psi_i(\vec{r})|^2, \tag{11}$$

where the sum in (11) is over bound and continuum states having single-particle energies $\varepsilon_i$ less than the chemical potential $\mu$. The energy $\overline{\Delta E}(\bar{n})$ can be written explicitly in terms of the self-consistent wave functions and energy eigenvalues of this noninteracting system.

In practice some approximate form for $E_{\mathrm{xc}}[n]$ must be chosen. Several workers have reported energies for light atoms in jellium using the local density approximation in which $E_{\mathrm{xc}}[n]$ is defined in terms of the exchange and correlation energy of a uniform electron gas. Results for H (Ref. 14), He (Refs. 15 and 16), and Li (Ref. 17) for a range of mean gas densities have appeared. The results of different authors are in agreement apart from some small differences due to different parameterizations of electron gas data which have been used. Given a specific form for $E_{\mathrm{xc}}[n]$ the numerical uncertainty in $\overline{\Delta E}(\bar{n})$ cannot be more than $\pm 2 \times 10^{-3}$ hartrees.

A generalization of the KS procedure to include spin polarization has been made by von Barth and Hedin.[18] Separate effective potentials for up- and down-spin electrons were introduced, and the dependence of $E_{\mathrm{xc}}$ on the spin polarization $\zeta(\vec{r}) = [n\uparrow(\vec{r}) - n\downarrow(\vec{r})]/n(\vec{r})$ as well as the density $n(\vec{r}) = n\uparrow(\vec{r}) + n\downarrow(\vec{r})$ was included. Using parametrized data for the ferromagnetic electron gas several authors[19] have treated H in spin-polarized jellium. Particle density and spin polarization distributions were reported but no impurity energies were given.

In the paramagnetic case, the impurity energy has been calculated either by direct substitution into the energy functional or by use of the Hellman-Feynman theorem and an integration over coupling constant $Z$. This latter method emphasizes the localized nature of the energy density associated with $\overline{\Delta E}$.[11] To interpret this energy it is convenient to visualize the insertion of the impurity as proceeding in three steps: (i) $Z$ electrons are added to the system with an expenditure of energy $Z\mu$, the excess charge residing on the surface of the jellium sample. (ii) The nucleus of charge $Z$ is inserted into the gas *without* allowing the electrons to relax in its presence. The energy change for this step is simply the energy $Z\Delta\phi$ required to surmount the electrostatic potential difference $\Delta\phi$ between the interior and exterior of the sample. (iii) Finally, the electrons in the sample relax to screen the impurity resulting in what may be termed the rearrangement energy $\Delta E_R$. Combining these terms gives the impurity energy $\overline{\Delta E} = \Delta E_R + Z\Delta\phi + Z\mu = \Delta E_R + Z\bar{\mu}$, where the second equality introduces the internal chemical potential of the electron gas. The rearrangement energy $\Delta E_R$ is analogous to the energy of the isolated impurity and through the Hellman-Feynman theorem can be expressed in terms of the screening charge density $\Delta n_Z(\vec{r})$ for various coupling constants $Z$. Both $\Delta E_R$ and $\bar{\mu}$ depend upon the local properties of the gas of density $\bar{n}$. In contrast, the thermodynamic potential, $\overline{\Delta\Omega} = \overline{\Delta E} - Z\mu$, on which most authors have concentrated is not a local quantity. The subtraction of $Z\mu$ removes from the expression the work done in adding $Z$ electrons but as a result, $\overline{\Delta\Omega} = \Delta E_R + Z\Delta\phi$ and so depends on a nonlocal property, namely, the potential energy difference $\Delta\phi$. For this reason it is preferable to base a theory on approximations to $\Delta E$ and not to $\Delta\Omega$. Tests of the UDA for impurities in nonuniform hosts described in the next section support this point of view.

We shall now show that in addition to the energy at a particular $\bar{n}$ a simple expression also exists for the slope of the energy curve $d\overline{\Delta E}/d\bar{n}$. This expression is made use of frequently in the following sections.

According to the theorem of Hohenberg and Kohn,[2] the density of an electronic system in the presence of an external potential $v(\vec{r})$ can be obtained from the variational principle

$$\frac{\delta\Omega_v[n]}{\delta n}=\frac{\delta(E_v[n]-\mu N)}{\delta n}=0\,. \tag{12}$$

In this form variations in the particle number $N$ are allowed. Again we are interested in the situation of a point charge with $\Delta n_Z^{+}(\vec{r})=Z\delta(\vec{r})$ in a uniform electron gas with $n_0^{+}(\vec{r})=\bar{n}$. The energy with and without the impurity will be denoted in the present argument by $E_{v_Z}[n_Z]$ and $E_{v_0}[\bar{n}]$, respectively. The impurity energy (8) is then

$$\overline{\Delta E}(\bar{n})=\Omega_{v_Z}[n_Z]-\Omega_{v_0}[\bar{n}]+Z\mu(\bar{n})\,, \tag{13}$$

where the argument of $\overline{\Delta E}$ emphasizes that a gas of density $\bar{n}$ is being considered. We now suppose that the density of the positive background is increased by a small amount, $\bar{n}\rightarrow\bar{n}+\delta\bar{n}$, with a corresponding increase in electron number to ensure charge neutrality. There results a change in the impurity density, $n_Z\rightarrow n_Z+\delta n_Z$, as well as in the external potentials, $v_0\rightarrow v_0+\delta v_0$ and $v_Z\rightarrow v_Z+\delta v_Z$. The impurity energy in this new situation is

$$\begin{aligned}\overline{\Delta E}(\bar{n}+\delta\bar{n})={}&\Omega_{v_Z+\delta v_Z}[n_Z+\delta n_Z]-\Omega_{v_0+\delta v_0}[\bar{n}+\delta\bar{n}]\\&+Z\mu(\bar{n}+\delta\bar{n})\,.\end{aligned} \tag{14}$$

But the explicit change in the energy functional is given by

$$\begin{aligned}E_{v_Z+\delta v_Z}[n]={}&E_{v_Z}[n]\\&+\int d\vec{r}_1\int d\vec{r}_2\,\frac{\delta\bar{n}[Z\delta(\vec{r}_2)+\bar{n}-n(\vec{r}_2)]}{r_{12}}\,,\end{aligned} \tag{15}$$

so that using (12) we obtain

$$\begin{aligned}\Omega_{v_Z+\delta v_Z}[n_Z+\delta n_Z]={}&\Omega_{v_Z}[n_Z]\\&+\int d\vec{r}_1\int d\vec{r}_2\,\frac{\delta\bar{n}[Z\delta(\vec{r}_2)+\bar{n}-n_Z(\vec{r}_2)]}{r_{12}}\\&-\frac{d\mu}{d\bar{n}}\delta\bar{n}(N_0+Z)+O(\delta\bar{n}^2)\,.\end{aligned} \tag{16}$$

Similarly,

$$\Omega_{v_0+\delta v_0}[\bar{n}+\delta\bar{n}]=\Omega_{v_0}[\bar{n}]-\frac{d\mu}{d\bar{n}}\delta\bar{n}N_0+O(\delta\bar{n}^2)\,. \tag{17}$$

Subtracting (17) from (16) and taking the limit $\delta\bar{n}\rightarrow 0$, we find

$$\frac{d\overline{\Delta E}}{d\bar{n}}=-\int d\vec{r}\,\phi_Z(\vec{r})\equiv-\bar{\phi}_Z\,, \tag{18}$$

where again $\phi_Z(\vec{r})$ is the localized Hartree potential of the impurity (5). Thus the slope of the $\overline{\Delta E}$-vs-$\bar{n}$ curve is given simply in terms of the mean Hartree potential of the quasiatom in a gas of density $\bar{n}$. Straightforwardly we have

$$\frac{d^2\overline{\Delta E}}{d\bar{n}^2}=-\int d\vec{r}\,\frac{d}{d\bar{n}}\phi_Z(\vec{r})=-\frac{d\bar{\phi}_Z}{d\bar{n}} \tag{19}$$

so that any curvature of the energy curve is related to variations of the mean Hartree potential with mean density. Such variations reflect the degree to which the quasiatom responds to changes in the ambient density.

The slope theorem (18) is exact and does not depend on specific assumptions for the energy functional (e.g., for $E_{\mathrm{xc}}[n]$). It can be proved by alternate methods such as those used by Budd and Vannimenus[20] in their derivation of various sum rules for the surface properties of jellium. On a practical level (18) is useful as a check of self-consistency in the solution of the impurity in jellium. Alternatively, it can be used to add detail to the $\Delta\bar{E}$-vs-$\bar{n}$ energy curve, since a single self-consistent calculation at a given $\bar{n}$ yields both $\overline{\Delta E}$ and its slope. Equations (18) and (19) will be used in the interpretation of the energy curves for the light impurities discussed in the next section and in the formal development of the uniform-density approximation for an impurity in a nonuniform host (Sec. V).

## IV. UDA FOR LIGHT ATOMS

Energy curves for some light atoms in jellium will now be presented, and their use in the UDA will be investigated for a few examples of nonuniform hosts. He, H, and Li will be considered in turn, this order corresponding to the increasing complexity of their interactions with the host. The self-consistent screening density and energy for these impurities in jellium have been recalculated using numerical algorithms described previously.[14] Self-consistency was achieved by the method of Manninen *et al.*[21] The local density approximation (LDA) was used in these calculations with the spin-dependent exchange-correlation energy function taken from the work of Gunnarsson and Lundqvist.[22] The general method for obtaining the energy curves is of course not dependent on the LDA and any improvements to $E_{\mathrm{xc}}[n]$ can be incorporated in future work.

### A. Helium

The energy curve for He in paramagnetic jellium is shown in Fig. 1. The fact that the curve is devoid of structure will be seen to be indicative of an inert atom. It increases monotomically with increasing mean electron density[23] [$\overline{\Delta E}(\bar{n})=-2.860+11.5\bar{n}-26.0\bar{n}^2$ a.u. fits the calculated points to a few millihartree], has little curvature, and, at low densities, tends towards the energy of the free atom as calculated within the Kohn-Sham method (−2.860 a.u. in agreement with Gunnarsson

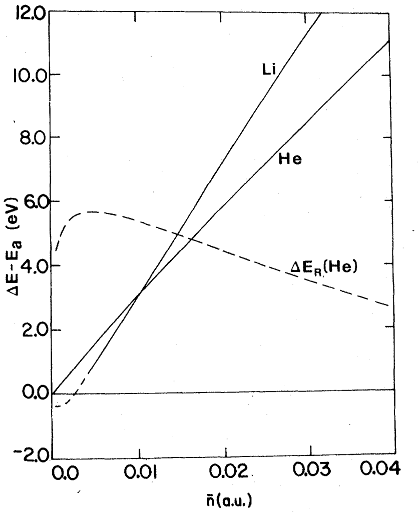

FIG. 1. Energy curves versus mean density $\bar{n}$ for He and Li relative to the free-atom energies [$-77.79$ eV for He (Ref. 22) and $-200.82$ eV for Li (Ref. 30)]. The relaxation energy $\Delta E_R$ for He is also shown relative to the free atom.

and Lundqvist[22]). Slopes of the energy curve calculated using numerical interpolation agree with values calculated from the exact relation (18) to 1% except at the highest mean densities considered where the discrepancy was 5%. We suspect that this was due to truncation of the integration in (18) rather than uncertainty in the energy values themselves.

The doubly occupied 1$s$ state is bound throughout the range of mean densities presented in Fig. 1 and merges with the conduction band only at the exceedingly high density corresponding to $r_s \approx 0.5$ a.u.. As found in previous atomic calculations[24] the Kohn-Sham 1$s$ energy eigenvalue for the free atom ($-0.583$ a.u.) lies considerably above the Hartree-Fock (HF) value ($-0.918$ a.u.).[25] In the electron gas the level is even shallower but more surprising is the substantial variation of the 1$s$ energy over the metallic density range, rising from $-0.445$ a.u. at $r_s = 4$ to $-0.346$ a.u. at $r_s = 2$. This shift is large enough to reduce the 1$s$ contribution to the screening charge density at the nucleus by 10%. Thus the assumption of a rigid ion core is not particularly good even for He, and ion pseudopotentials formulated within the KS theory which assume a rigid core bear some reexamination. The decrease in core density near the nucleus with increasing host density is compensated by an increase in the contribution from the perturbed continuum (or scattering) states, which leads to a net increase in the total displaced density shown in Fig. 2. However, the inertness of the free atom is reflected in the total quasiatom density through its relative insensitivity to the mean host density.

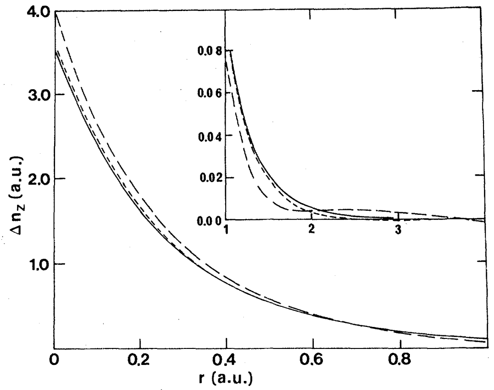

FIG. 2. Screening charge density as a function of the distance from an He nucleus in jellium ($r_s = 1.6$, long-dashed curve; $r_s = 4.0$, short-dashed curve). The free-atom density is shown as the solid curve. The inset shows the densities beyond $r = 1.0$ a.u. on an expanded scale.

Another aspect which demonstrates the rigidity of the He quasiatom is the rearrangement energy $\Delta E_R = \overline{\Delta E}(\bar{n}) - Z\bar{\mu}(\bar{n})$, which is shown in Fig. 1. Except at very low mean densities this varies less rapidly with $\bar{n}$ than $\overline{\Delta E}$. In view of the behavior of the rearrangement energy $\Delta E_R$, the strong increase in $\overline{\Delta E}$ with mean density can be attributed to the increasing energy required to insert two extra electrons into the electron gas. This rate of increase can alternatively be considered in terms of the mean Hartree potential of the quasiatom, Eq. (18). It is of interest to observe that the value of the mean potential in the metallic density range ($\bar{\phi}_Z \simeq -11.4$ a.u.) is quite different from the value for the free atom ($\bar{\phi}_{\mathrm{He}} = -5.34$ a.u.). The difference is due to the outward relaxation of the atomic screening cloud when the atom is placed in a metallic environment. The mean Hartree potential is a direct measure of this relaxation, since it can be expressed as a radial moment of the screening charge density

$$\bar{\phi}_Z = -\frac{(4\pi)^2}{6}\int_0^\infty dr\, r^4\, \Delta n_Z(r)\,, \tag{20}$$

which is particularly sensitive to the oscillations of the density in the outer regions of the quasiatom.[26] Presumably the mean quasiatom potential will tend to the atomic value in the low-density limit. However, in the metallic density range its variation with mean density is small and the lack of curvature in the energy curve is another measure of the inertness of the He quasiatom. Linear energy curves are to be expected for any inert atom.

The UDA for the quasiatom has been tested by comparing the results of (9) with results, exact within the KS method, for simple nonuniform hosts. Some comparisons were made in I between the UDA and a few results for H, He, and Li situated at the center of a vacancy in jellium. We have carried out more extensive calculations for a range of mean densities and vacancy valencies.

A vacancy in jellium is taken to mean merely a spherical hole in the positive background so that

$$n_0^+(\vec{r}) = \bar{n}\Theta(r-R)\,, \tag{21}$$

where the unit step function $\Theta(x)=1$ if $x>0$ and zero otherwise and where the valence $Z_v$ is defined through $\frac{4}{3}\pi R^3\bar{n} = Z_v$. This model has been used extensively as a basis for calculations of monovacancy formation energies for metals.[21] The electron-density distribution and energy can be computed exactly within the KS method. This nonuniform system is the host. The problem with an atom at the center of the vacancy can also be solved, and the energy difference $E_B$ between the atom in the vacancy and the atom in the bulk jellium detached from the vacancy can be calculated. Calculations of this sort were first performed by Manninen *et al.*[17] and by Nørskov.[16]

If $n_0(\vec{r})$ is the electron density for a vacancy in jellium, then the UDA for the quasiatom gives simply

$$E_B^{\text{UDA}} = \overline{\Delta E}(n_0(0)) - \overline{\Delta E}(\bar{n})\,. \tag{22}$$

Results of the UDA (22) and of the "exact" calculations for He impurities are given in Table I. There is binding to the vacancy in all cases, the He atom preferring the low-electron-density region in the vacancy in accordance with the positive slope of $\overline{\Delta E}(\bar{n})$ (Fig. 1). Bearing in mind the simplicity of the UDA there is good agreement (~10%) though it tends to be poorer at the highest densities which are substantially above the metallic range. Figure 3, in which the exact results are plotted against the results of the UDA, illustrates the overall situation.

The results of a possible alternative approximation scheme are also shown in Fig. 3. In this method one makes a uniform-density approximation for the rearrangement energy $\Delta E_R$, rather than for the quasiatom energy $\Delta E$, i.e.,

$$\overline{\Delta E}'(n_0(0)) = \Delta E_R(n_0(0)) + Z(\mu + \phi(0))\,. \tag{23}$$

The exact electrostatic potential of the host at the position of the impurity, $\phi(0)$, now appears. Since the chemical potential in the bulk of the sample is given by $\mu = \bar{\mu}(\bar{n}) - \phi(\infty)$, the difference in the two approximations is

$$\overline{\Delta E}'(n_0(0)) - \overline{\Delta E}(n_0(0)) = Z(\bar{\mu}(\bar{n}) - \phi(\infty)) - Z(\bar{\mu}[n_0(0)] - \phi(0))\,. \tag{24}$$

As shown in Fig. 3 this difference leads to a large discrepancy in the calculated impurity-vacancy binding energy $E_B'$. It can therefore be inferred that the Thomas-Fermi approximation which assumes that the constant chemical potential $\mu$ is everywhere equal to $\bar{\mu}(n(\vec{r})) - \phi(\vec{r})$ cannot be valid in this situation, otherwise there would be no distinction between $E_B$ and $E_B'$. This also emphasizes the importance of keeping the quasiatom as a neutral unit. Not only are large electrostatic energies such as $Z\phi(0)$ eliminated but also the additional $Z$ electrons are localized and only sample the immediate environment of the impurity [leading to $Z\bar{\mu}(n_0(0))$ implicit in (9) rather than $Z\bar{\mu}(\bar{n})$ in (23)].

The success of the UDA for He does not seem to be restricted to just lower-density regions of

TABLE I. Binding energies (eV) of He in jellium vacancies. $Z_v$ is the valence of the vacancy. Densities are in atomic units.

| $Z_v$ | $r_s$ | $\bar{n}$ | $n_0(0)$ | $\bar{n}_0(0)$ [Eq. (54)] | $\Delta E_{es}$ [Eq. (53)] | $E_B^{\text{UDA}}$ [Eq. (22)] | $E_B$ [Eq. (33)] | $E_B$ [Eq. (56)] | $E_B^{\text{exact}}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.6 | 0.058 28 | 0.026 17 | 0.037 40 | −4.65(−4.62) | −8.19 | −8.40 | −9.82 | −9.87 |
| | 2.0 | 0.029 84 | 0.011 57 | 0.016 73 | −2.37 | −4.92 | −5.63 | −5.88 | −6.04 |
| | 3.0 | 0.008 84 | 0.002 43 | 0.003 51 | −0.71 | −1.96 | −2.42 | −2.34 | −2.26 |
| | 4.0 | 0.003 73 | 0.000 73 | 0.000 87 | −0.33 | −0.90 | −1.17 | −1.20 | −1.03 |
| 2 | 1.6 | 0.058 28 | 0.017 53 | 0.028 34 | −4.46 | −10.5 | −11.5 | −12.1 | −11.7 |
| | 2.0 | 0.029 84 | 0.007 20 | 0.011 67 | −2.20 | −6.28 | −7.29 | −7.13 | −7.07 |
| | 3.0 | 0.008 84 | 0.001 26 | 0.001 93 | −0.65 | −2.31 | −2.83 | −2.77 | −2.58 |
| | 4.0 | 0.003 73 | 0.000 32 | 0.000 48 | −0.27 | −1.03 | −1.28 | −1.25 | −1.17 |
| 3 | 1.6 | 0.058 28 | 0.013 09 | 0.022 75 | −3.70 | −11.7 | −12.7 | −12.9 | −13.0 |
| | 2.0 | 0.029 84 | 0.005 07 | 0.008 86 | −1.69 | −6.94 | −7.75 | −7.45 | −7.53 |
| | 3.0 | 0.008 84 | 0.000 76 | 0.001 30 | −0.60 | −2.48 | −2.99 | −2.91 | −2.67 |
| | 4.0 | 0.003 73 | 0.000 17 | 0.000 30 | −0.19 | −1.06 | −1.25 | −1.22 | −1.20 |

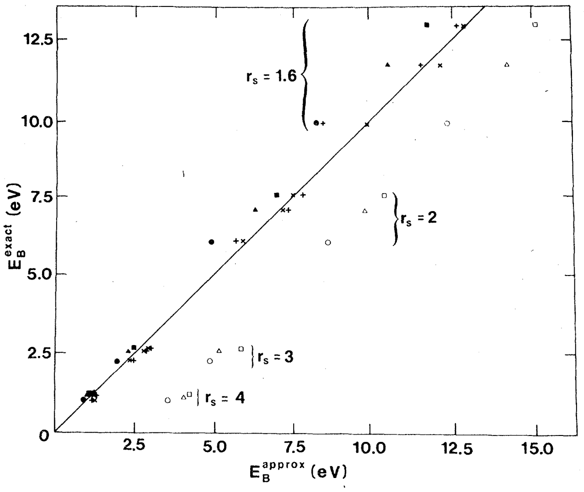

FIG. 3. Comparison of the exact binding energies of He to a jellium vacancy with calculations based on various approximations. The solid line represents exact agreement. For each value of $r_s$ indicated, the horizontal group of points bracketed by circles, triangles, and squares corresponds to a jellium vacancy of valence $Z_v = 1$, 2, and 3, respectively. The solid points are obtained using the UDA [Eq. (22)] while the open points are based on (23). The + and × signs in each group give the corrections to the UDA using the gradient expansion (33) and (34) and the sampling ansatz (56), respectively.

the host. One test has been made in which $Z_v < 0$ and the host electron density is piled up above the background. For $Z_v = -1$ and $r_s = 1.6$ the UDA gives $E_B = +0.369$ a.u. in perhaps fortuitously good agreement with the "exact" result $E_B = +0.368$ a.u.

### B. Hydrogen

The energy curve for H in paramagnetic jellium is shown in Fig. 4. A fairly linear rise at high mean densities, similar to the case of He, is seen. This again originates largely from the cost in energy to insert an extra electron. However, the displaced charge around the proton is more sensitive to mean density than in the He case and consequently the energy curve has more curvature. The minimum in the energy curve is a new qualitative feature.

Recalling the exact expression for the slope of the energy curve (18), the minimum clearly indicates the changing structure of the quasiatom. This change has its origin in the formation of a doubly occupied 1$s$ bound state for $\bar{n} \lesssim 0.03$ a.u., observed by previous authors,[14] after which the screened proton begins to resemble an $H^-$ ion. This results in the growth of the first positive maximum in the Hartree potential as the mean density is reduced until eventually at $\bar{n} \simeq 0.0025$ a.u. ($r_s = 4.6$), the mean value of the Hartree potential goes through zero and the slope of the energy curve changes sign.

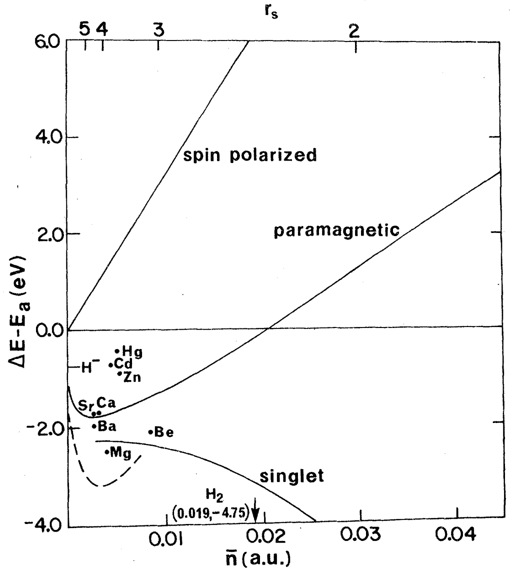

FIG. 4. Energy curves versus mean density $\bar{n}$ for H for various spin polarizations as described in the text, relative to the free-atom energy −13.38 eV.[30] The dashed curve is the limiting low-density result given by Eq. (25). The ordinates of the points correspond to the energy of H in the $M$H molecules while the abscissas denote the density of the $M$ atom at the equilibrium spacing $R$ of the molecule. The molecular parameters are obtained from Ref. 34. The atomic densities are obtained from Ref. 33. The corresponding point (Ref. 35) for the ground state of $H_2$ is indicated by the arrow. The energy of $H^-$ is also shown (Ref. 32).

The correct low-density limit for H is the $H^-$ ion rather than the neutral free atom, since there is a positive electron affinity for the atom and the electron gas chemical potential becomes vanishingly small. Strictly speaking, this limit, as well as that of other negative ions, cannot be reached using the LDA in the density-functional theory[27,28] but for the range of densities considered here this failure is of no consequence. Taking $H^-$ as the low-density limit, it follows from the slope theorem (18) that the energy curve approaches $E_{H^-}$ from below and has infinite slope at $\bar{n} = 0$. The following simple model accounts rather well for the form of the energy curve in the low-density region. In the absence of the impurity the electron gas at very low densities forms a Wigner lattice with each electron oscillating in the harmonic potential $V(r) = \frac{1}{2} r^2 / r_s^3$ a.u. at the frequency $\omega_0 = r_s^{-3/2}$ corresponding to a ground-state energy $\epsilon_0 = \frac{3}{2}\omega_0$. An impurity H atom will sit at some Wigner lattice site and will combine with the electron there to form an $H^-$ ion perturbed by the potential $V(r)$. Treating the perturbation to first order we have

$$\Delta E \simeq E_{\mathrm{H}^-} + \tfrac{2}{3}\pi\bar{n}\langle r^2\rangle - (3\pi\bar{n})^{1/2}, \qquad (25)$$

where $\langle r^2\rangle$ is the expectation value of $r^2$ for $\mathrm{H}^-$. $\Delta E$ given by (25) approaches $E_{\mathrm{H}^-}$ vertically from below as required. Using a variational HF wave function to evaluate $\langle r^2\rangle$ $[\varphi_{1s}(\vec{r}) = (\alpha^3/\pi)^{1/2}e^{-\alpha r}$ with $\alpha = \frac{11}{16}]$ there is a minimum at $\bar{n} = 0.0033$ a.u. as shown in Fig. 4, but the minimum is too deep. The reason for this is that the Wigner model is not applicable for densities near the minimum in the energy curve. The electrons are delocalized and so the second term in (25) will be modified by screening and the third term will be more closely related to the bulk chemical potential rather than the Einstein oscillator energy as in (25). Nevertheless, the qualitative success of this simple model suggests that the energy curve will have a minimum for all atoms with electron affinities; the minima for O, the halogens, etc., are likely to be very pronounced. A minimum means that the quasiatom has maximum stability at some finite electron density which in the case of H is about $\bar{n} \simeq 0.0025$ a.u.

The vacancy test of the UDA was also applied to H impurities in I using previously published data.[16,17] A few additional calculations for $Z_v = 1$ vacancies have been made confiriming the overall picture reported in I, and all the available results are summarized in Table II. The agreement between the UDA and exact calculations is slightly poorer for H than for He, but a new qualitative feature emerges which is accurately portrayed by the UDA. At high mean densities $E_B < 0$, the low-density region in the vacancy being preferred because of the positive slope of the energy curve. However at lower mean densities $E_B$ becomes smaller in magnitude and changes sign at about Na mean density at which point H is more stable in the bulk than in the vacancy. This coincides with the minimum in the energy curve and is a consequence of it.

A further test of the UDA has been made for the problem of H chemisorption on a jellium surface. The ingredient for the UDA calculation is the surface-electron-density profile $n_0(z)$ as calculated by Lang and Kohn.[29] Here $z$ is the distance from the edge of the positive jellium background. A number of calculations of H chemisorption in this model have been reported[5,6] and the most recent results[6] for $r_s = 2.07$ a.u. corresponding to Al and for $r_s = 3.99$ (Na) are illustrated in Fig. 5. Also shown are the results of the UDA for $r_s = 2$ and 4. All energies in the figure are with respect to the KS spin-polarized H atom $[E_a = -13.38$ eV (Ref. 30)].

TABLE II. Binding energies (eV) of H in jellium vacancies. Densities are in atomic units.

| $Z_v$ | $r_s$ | $\bar{n}$ | $n_0(0)$ | $E_B^{\mathrm{UDA}}$ | $E_B^{\mathrm{exact}}$ |
|---|---|---|---|---|---|
| 1 | 1.6 | 0.058 28 | 0.026 17 | −4.1 | −5.5 |
| | 2.0 | 0.029 84 | 0.011 57 | −2.3 | −3.3 |
| | 3.25 (Li) | 0.007 0 | 0.001 8 | −0.23 | 0.0[a] |
| | 3.93 (Na) | 0.003 9 | 0.000 8 | +0.11 | 0.6[b] |
| 2 | 2.65 (Mg) | 0.012 8 | 0.002 2 | −0.85 | −1.0[a] |
| 3 | 2.07 (Al) | 0.026 9 | 0.004 3 | −2.6 | −3.1[b] |

[a] Reference 17.

[b] Reference 16.

In the case of Al the minimum in the "exact" curve occurs at a distance $z = 0.8$ a.u. outside the jellium surface and is qualitatively reproduced by the UDA ($z_{\min} = 1.65$ a.u.). As the H quasiatom is moved through the surface the local density decreases from the bulk value $\bar{n} \simeq 0.03$ a.u. and its energy decreases until a point is reached at which the local density gives maximum stability. The depth of the minimum with respect to the energy in the bulk is given well by the UDA. However, the UDA breaks down at large separations, giving the dissociation product $\mathrm{H}^-$ rather than H, which is incorrect since the energy required to remove an electron from the semi-infinite jellium (3.9 eV for $r_s = 2$ as reported by Lang and Kohn[31]) is greater than the H electron affinity [0.75 eV (Ref. 32)]. The interaction of the H quasiatom with the surface must in these circumstances be nonlocal. The addition of the electrostatic energy in (4) to the UDA should improve matters since $\phi_Z(r)$ becomes long ranges as $\bar{n}$ decreases, as evidenced by the large negative slope of the energy curve [see Fig. 4 and (18)]; however, this can only delay the breakdown and further work is needed to resolve this problem.

The results for a low-density electron gas cor-

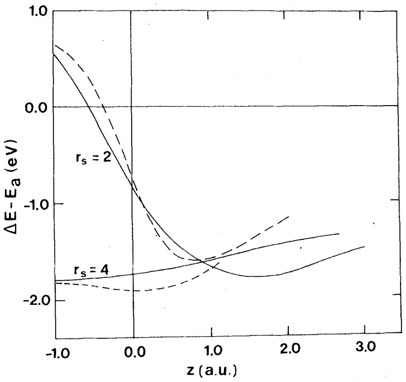

FIG. 5. Chemisorption energies for H at a jellium surface versus distance from the edge of the jellium background. The solid lines are based on the UDA while the dashed lines are taken from Ref. 6.

responding to Na ($r_s=3.99$) are equally well reproduced by the UDA. In this case the chemisorption curve is rather flat with only a very shallow minimum near $z=0.0$ a.u., while in the UDA the minimum is again shallow and displaced to $z=-1$ a.u. These results can easily be understood in terms of the quasiatom energy curve. Since the bulk density is close to the minimum in the energy curve, the large change in host density experienced by the quasiatom as it is moved through the surface gives rise to a comparatively small change in energy.

The UDA for H has also met with some success in treating the diatomic *M*H molecules where *M* is a group-II metal atom. We regard the metal atom as the host and form the molecule by placing an H quasiatom in the paramagnetic electron density $n_0(\vec{r})$ of the free *M* atom. In Fig. 4 points representing the molecule are plotted where their coordinates are—the local electron density of the free *M* atom $n_0(\vec{R})$ (Ref. 33) at the observed internuclear separation *R*, and the observed binding energy of the molecule.[34] The points for all these molecules are clustered around the point of maximum stability of the H quasiatom, so clearly the model has some relevance for molecules. However, this simplest of quasiatom models is not entirely satisfactory. A more quantitative model must account for the electrostatic interaction in (4) and the effect of local density gradients. These must also be included if the model is to be symmetric so that it is irrelevant which of *M* or H is treated as the host and which as the quasiatom. As in the H chemisorption case discussed above the UDA will break down at large internuclear separations as the interaction becomes nonlocal.

We have also considered $H_2$. Electrostatic interactions and density gradient corrections should be no larger than in the *M*H molecules, and yet the point corresponding to $H_2$ has coordinates[35] (0.019 a.u., −4.752 eV) which is far from the minimum and well off Fig. 4. The resolution of this problem lies in the complete spin polarization of the host, in this case simply a free H atom, to which the H quasiatom is added. In a general application of the UDA the quasiatom energy as a function of local spin polarization, $\bar{\zeta}$ as well as local density will be required. In the particular case of $H_2$ we require $\overline{\Delta E}(\bar{\zeta},\bar{n})$ with $\bar{\zeta}=1$.

We have performed self-consistent KS calculations of the energy of H in ferromagnetic jellium. Two physically distinct cases emerge. Consider H in paramagnetic jellium with the application of a slowly increasing external magnetic field $B_0$. In this process the energies of the up and down spin states shift relative to each other and, in order to maintain a common chemical potential for both spin components, a net spin polarization develops having a value $\bar{\zeta}=(\bar{n}_\uparrow-\bar{n}_\downarrow)/(\bar{n}_\uparrow+\bar{n}_\downarrow)$ far from the impurity. For $\bar{n}\lesssim 0.03$ a.u. there is a doubly occupied 1*s* state which is also influenced by the spin polarization. The majority-spin bound state becomes less tightly bound (with respect to the bottom of the majority-spin continuum), and minority spins begin to dominate in the screening cloud. The situation is illustrated schematically in Fig. 6. If $\bar{\zeta}$ is increased, the majority-spin bound state eventually merges with the continuum, leaving only a minority-spin 1*s* state and the minority-spin polarization of the screening cloud becomes more dominant. This behavior was correctly reported by Jena *et al.*[19] but these authors incorrectly concluded that the screening cloud must contain one majority spin for the extreme case of $\bar{\zeta}=1$ when the jellium is completely spin polarized. This is correct only for $B_0$ large enough to raise the minority bound state above the up-spin Fermi level. This case, in which the quasiatom has its spin parallel to the jellium, gives the energy curve labeled "spin polarized" in Fig. 4. However, before this situation is reached, there is a range of $B_0$ for which the jellium is completely polarized, the minority-spin 1*s* bound state is occupied, and the screening cloud contains one minority spin. This "singlet" state in which the quasiatom has spin antiparallel to the jellium is also shown in Fig. 4. For $\bar{n}\gtrsim 0.03$ a.u. there are no bound states and only the spin-polarized case is possible. We were unable to obtain self-consistent solutions for the "singlet" case for $\bar{n}<0.004$ a.u. We are not sure how to interpret the "singlet" state but believe that it might be a poor attempt by the quasiatom to reproduce the conditions existing in the singlet ground state of $H_2$.

The spin-polarized case is easier to interpret. The energy curve has the same inert atom characteristics as the He energy curve in Fig. 1. The increase with increasing density is almost all due to the energy cost to insert an extra electron and

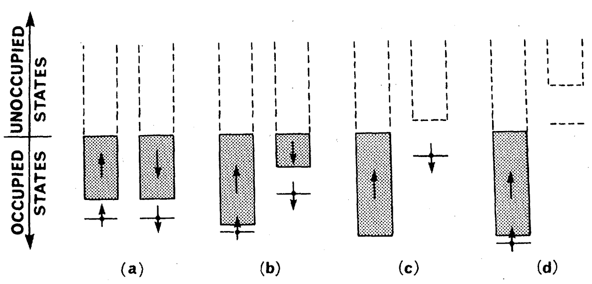

FIG. 6. Schematic fugure of the occupied electronic states for H in jellium for increasing spin polarization: (a) paramagnetic state, (b) intermediate spin polarization, (c) singlet state, and (d) spin-polarized case.

the linearity reflects the rigidity of the quasiatom. In the limit of low mean density the quasiatom tends towards a neutral H atom [numerical extrapolation gives $\overline{\Delta E}(0) = -13.37$ eV in good agreement with the result of Gunnarsson *et al.*[30] for the spin-polarized free H atom, $-13.38$ eV]. In a strictly up-spin environment an up-spin H atom has effectively a closed 1*s* shell.

Although we are unable to treat the $H_2$ ground state at the moment, the spin-polarized energy curve with the UDA can be used to study the lowest triplet $H_2$ state, $^3\Sigma_u^+$. Accurate results[35] for the energy of this state as a function of internuclear separation are shown in Fig. 7 along with the results of the UDA obtained by placing an up-spin quasiatom in the local up-spin electron density of a free H atom. There is remarkably good agreement, perhaps, because in this case nonlocal interaction effects should be minimal, the correct limit at large separation being obtained in the local approximation. Of course the van der Waals minimum will not be reproduced by the UDA.

### C. Lithium

The energy curve for Li has been calculated in the range $1.6 \leq r_s \leq 6$ and the results are also shown in Fig. 1. The dashed portion of the curve should be regarded as an upper bound, since thoroughly converged results were not obtained in this range. The curve is shifted upwards in energy by approximately 3 eV with respect to the curve presented earlier in I. There are two components to this shift. Firstly, the value of the KS Li atom ground-state energy reported by Manninen *et al.*[17] and used in I ($-7.30$ a.u.) differs from the result of the full spin-polarized calculation of Gunnarsson *et al.*[30] ($-7.383$ a.u.) which is used here. Secondly, there is also a discrepancy of $\simeq 1$ eV in the $\overline{\Delta E}$ results themselves.

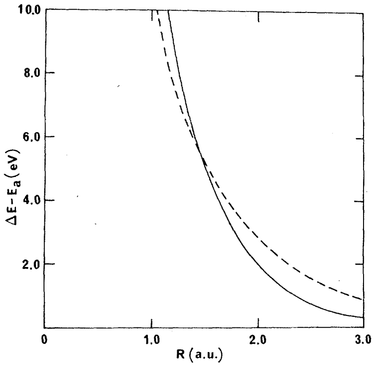

FIG. 7. Energy of the triplet $^3\Sigma_u^+$ state of $H_2$ vs internuclear separation. The solid line is the UDA and the dashed line is an accurate variational estimate (Ref. 35).

Since our results for $\overline{\Delta E}$ are consistent with the slopes calculated using Eq. (18), it appears that there is a systematic error in the earlier work.[17] Nevertheless, the general features are unaltered, and the energy curve retains its qualitative similarity to that of H in a paramagnetic gas. At low density $\overline{\Delta E} < E_a$ for Li and there is an indication of a shallow minimum at some density less than 0.001 a.u. The presence of a minimum is expected, since free $Li^-$ is stable. The simple Wigner lattice model presented earlier would predict a minimum which is shallower than that for H and shifted to lower density, because the electron affinity for Li (Ref. 36) is about $\frac{2}{3}$ that for H and presumably $\langle r^2 \rangle$ is larger for the more loosely bound $Li^-$. However, the energy curve could be in error at densities $\lesssim 0.001$ because of the breakdown of the LDA which does not give a bound $Li^-$, and the actual minimum is likely to be deeper and at a higher density than is indicated in the figure.

It is of interest to note that the slope of the energy curve for Li at higher densities ($n \gtrsim 0.03$ a.u.) is about a factor $\frac{3}{2}$ larger than for He. This is what one might expect if the rearrangement energy [see Sec. IV A] were independent of density in which case the slope would be $Z d\overline{\mu}/d\overline{n}$. The actual slopes are reduced by about 25% from this value reflecting the density dependence of $\Delta E_R$, which is shown for He in Fig. 1. That this scaling of the slope with the atomic number $Z$ cannot persist to higher values of $Z$ (Ref. 37) can be inferred from the slope theorem. Being more tightly bound to the nucleus, core states will tend to make a smaller contribution to the mean Hartree potential than valence (or continuum) states so that the slope is in some way characteristic of these more loosely bound orbitals. This tendency to reflect the properties of the valence states should be even more evident in the curvature of the energy curve since the core states are relatively rigid.

The amount of *p*-wave screening found for the Li quasiatom is perhaps surprising. By analogy with the situation for H, it would be expected that the tendency at low densities toward $Li^-$ with the appearance of a doubly occupied 2*s* state would be foreshadowed by the predominance of *s*-like screening. In fact, in the range of densities ($1.6 \leq r_s \leq 4$) where thoroughly converged results have been obtained, the total screening cloud containing three electrons consists of the two 1*s* electrons and a third from the continuum which is almost completely *p*-like. The *p*-wave scattering at conduction-band energies is clearly large for Li. It is well known that the Li *p*-wave pseudopotential is larger than that of the other alkalis because there are no *p* states in the core to orthogonalize to, however, the magnitude of the effect of this on the density is unexpected.

The minimum in the energy curve for Li corresponds to the point of maximum stability of the quasiatom and indicates that Li will chemisorb at metal surfaces but at larger separations than for H. This is consistent with previous results[38] on alkali chemisorption.

In view of the difference of the present Li energy curve from that reported in I, Li-vacancy binding energies have been recalculated and the results are presented in Table III. The UDA estimates are in somewhat better agreement with the exact results[17] because of the lower values of $\overline{\Delta E}$ (relative to the bulk energy) in the low-density region. As an independent check of the exact energies, a self-consistent solution for a Li atom in a vacancy ($r_s = 3.28$) was obtained which confirms the earlier value.

As a final application of the Li energy curve we consider its relationship to the metallic cohesive energy. The experimental quasiatom energy for a Li atom in a Li vacancy can be extracted from the experimentally determined cohesive energy, $E_c$ [$-1.63$ eV (Ref. 36)], and vacancy formation energy, $E_v$ [0.34 eV (Ref. 39)]. Consider constructing a metallic sample of $(N+1)$ atoms through the following cycle starting from $N$ Li atoms on $N$ sites in a piece of metal and one free Li atom. The energy of this system is, by definition of the cohesive energy, $(N+1)E_a + NE_c$, where $E_a$ is again the free-atom energy. At the cost of the Li monovacancy formation energy $E_v$ an atom can be taken from the interior of the metal and placed on the surface. Finally a metallic sample of $(N+1)$ atoms is obtained by placing the single free Li atom on the vacant site. This last change in energy is $(\Delta E - E_a)$ where, according to our definition, $\Delta E$ is just the quasiatom energy in the vacancy. The final energy of the system $(N+1)(E_a + E_c)$ must be equal to $(N+1)E_a + NE_c + E_v + (\Delta E - E_a)$, i.e., $\Delta E - E_a = E_c - E_v = -2.0$ eV. Using the electron density $n_v(0) = 0.001\,65$ a.u. at the center of a vacancy in $r_s = 3.28$ jellium, the UDA gives the value $\overline{\Delta E}(n_v(0)) - E_a = -0.3$ eV. However, as shown by the first entry in Table III, the UDA overestimates the quasiatom energy in the vacancy by 1.8 eV and so the "exact" quasiatom energy for the jellium model is $\Delta E - E_a = -2.1$ eV in good agreement with the experimental value. The difference between the UDA and the exact value is attributable to the inhomogeneities in the host density, corrections for which are discussed in the following section. However, it is apparent that the quasiatom picture is relevant to the cohesive properties of metals and may possibly find application in considerations of alloy stability.

TABLE III. Binding energies (eV) of Li in jellium vacancies. Densities are in atomic units.

| $Z_v$ | $r_s$ | $\overline{n}$ | $n_0(0)$ | $E_B^{\mathrm{UDA}}$ | $E_B^{\mathrm{exact}}$ |
|---|---|---|---|---|---|
| 1 | 3.28 | 0.0068 | 0.0017 | $-1.9$ | $-3.7$ |
| 1 | 3.25 | 0.0070 | 0.0018 | $-2.2$ | $-4.0$[a] |
| 2 | 2.65 | 0.0128 | 0.0022 | $-4.4$ | $-7.5$[a] |
| 3 | 2.07 | 0.0269 | 0.0043 | $-9.1$ | $-13.5$[a] |

[a] Reference 17.

## V. CORRECTIONS TO THE UDA

The simple approximation considered so far in which the electrostatic interaction of the quasiatom with the host charge distribution was neglected and where the quasiatom self-energy was assumed to depend only on the local host electron density met with good qualitative success in a variety of situations. In this section we investigate the reasons for this success by considering the impurity energy for a host in which the electron density inhomogeneities are small and can therefore be treated by perturbation theory. This approach suggests approximate methods for correcting the UDA and indicates the way in which the quasiatom samples the host density in its vicinity.

We consider a neutral host system that differs from a uniform jellium by the addition of a small positive charge distribution $\delta n_0^+(\vec{r})$ which satisfies $|\delta n_0^+(\vec{r})/\overline{n}| \ll 1$. The spatial distribution of this density is for the moment arbitrary. The electron density in this situation will be denoted by $n_0(\vec{r}) = n_0^{(0)} + n_0^{(1)}(\vec{r}) + \cdots$, where the superscripts refer to the order in the perturbation $\delta n_0^+(\vec{r})$. For example, the lowest order term is $n_0^{(0)} \equiv \overline{n}$. The total energy of the host correct to second order in the perturbation is

$$E_0 = E_0^{(0)} - \tfrac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \, \frac{n_0^{(1)}(\vec{r}_1)\,\delta n_0^+(\vec{r}_2)}{r_{12}} + \tfrac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \, \frac{\delta n_0^+(\vec{r}_1)\,\delta n_0^+(\vec{r}_2)}{r_{12}}, \qquad (26)$$

where $E_0^{(0)}$ is simply the energy of the unperturbed gas.

We now consider the analogous situation in which the perturbation is made to a system consisting of the jellium host, an impurity of charge $Z$, and $Z$ additional electrons so that the system is electrically neutral. The electron density will be denoted by $n_Z(\vec{r}) = n_Z^{(0)}(\vec{r}) + n_Z^{(1)}(\vec{r}) + \cdots$, where again the superscripts on the sequence of terms refer to the order in the perturbation. It will also be convenient in the following to develop a similar perturbation expansion for the impurity screening cloud, $\Delta n_Z(\vec{r}) = n_Z(\vec{r}) - n_0(\vec{r}) = \Delta n_Z^{(0)}(\vec{r}) + \Delta n_Z^{(1)}(\vec{r}) + \cdots$, and the electrostatic potential of the impurity,

$$\phi_Z(\vec{r}) = \int d\vec{r}\,'[\Delta n_Z(\vec{r}\,') - \Delta n_Z^{+}(\vec{r}\,')]/|\vec{r} - \vec{r}\,'|$$
$$= \phi_Z^{(0)}(\vec{r}) + \phi_Z^{(1)}(\vec{r}) + \cdots .$$

With these definitions the total energy of the host plus impurity system can be written to second order in the perturbation as

$$E_Z = E_0^{(0)} + \overline{\Delta E}(n_0^{(0)}) - \int d\vec{r}\,\phi_Z^{(0)}(\vec{r})\delta n_0^{+}(\vec{r})$$
$$-\tfrac{1}{2}\int d\vec{r}\,\phi_Z^{(1)}(\vec{r})\delta n_0^{+}(\vec{r})$$
$$+\tfrac{1}{2}\int d\vec{r}_1\int d\vec{r}_2\,\frac{\delta n_0^{+}(\vec{r}_1)\delta n_0^{+}(\vec{r}_2)}{r_{12}} . \tag{27}$$

The impurity energy (4), also correct to second order, is the difference between (27) and (26),

$$\Delta E = \overline{\Delta E}(n_0^{(0)}) - \int d\vec{r}\,\phi_Z^{(0)}(\vec{r})\delta n_0^{+}(\vec{r})$$
$$-\tfrac{1}{2}\int d\vec{r}\,\phi_Z^{(1)}(\vec{r})\delta n_0^{+}(\vec{r}) . \tag{28}$$

Our objective will be to infer a nonperturbative expression for the energy starting from this perturbation expansion.

In order to achieve this aim it is necessary, from a comparison with the general expression (4), to isolate those terms in (28) contributing to the electrostatic interaction $\Delta E_{\text{es}}$ between the neutral quasiatom and the neutral host. Doing so allows one to treat the electrostatic interactions in a rigorous way while permitting approximations to be made to the quasiatom self-energy. With

$$\Delta E_{\text{es}} \equiv \int d\vec{r}\,\phi_Z(\vec{r})[n_0(\vec{r}) - n_0^{+}(\vec{r})]$$
$$= \int d\vec{r}[\phi_Z^{(0)}(\vec{r}) + \phi_Z^{(1)}(\vec{r}) + \cdots]$$
$$\times[n_0^{(1)}(\vec{r}) + n_0^{(2)}(\vec{r}) + \cdots - \delta n_0^{+}(\vec{r})] \tag{29}$$

we have after some manipulation the following convenient form:

$$\Delta E = \Delta E_{\text{es}} + \overline{\Delta E}(n_0^{(0)}) - \int d\vec{r}\,\phi_Z^{(0)}(\vec{r})[n_0^{(1)}(\vec{r}) + n_0^{(2)}(\vec{r})]$$
$$-\tfrac{1}{2}\int d\vec{r}\,\phi_Z^{(1)}(\vec{r})n_0^{(1)}(\vec{r})$$
$$+\tfrac{1}{2}\int d\vec{r}\,\phi_Z^{(1)}(\vec{r})[\delta n_0^{+}(\vec{r}) - n_0^{(1)}(\vec{r})] . \tag{30}$$

The second-order contribution to the host density, $n_0^{(2)}$, appearing in (30) cancels with another concealed in $\Delta E_{\text{es}}$ [see Eq. (29)].

The second and subsequent terms on the right of (30) constitute the self-energy of the quasiatom identified in (4). To make contact with the UDA we must rewrite (30) so that the second term on the right makes reference only to the total host density $n_0^{(0)} + n_0^{(1)} + \cdots$. By doing so the artificial jellium starting point can be eliminated, and the resulting expression can be applied to systems for which the conditions of the present derivation are not met (for instance, to hosts where the nonuniformities are large). By expanding the UDA expression for the impurity energy about the unperturbed density, we obtain

$$\overline{\Delta E}(n_0(0)) = \overline{\Delta E}(n_0^{(0)} + n_0^{(1)}(0) + n_0^{(2)}(0) + \cdots)$$
$$= \overline{\Delta E}(n_0^{(0)}) - \overline{\phi}_Z^{(0)}(n_0^{(1)}(0) + n_0^{(2)}(0) + \cdots)$$
$$-\frac{1}{2}\frac{d\overline{\phi}_Z^{(0)}}{d\overline{n}}n_0^{(1)}(0)^2 - \cdots , \tag{31}$$

where we have used (18) and (19) to replace the density derivatives of the energy in favor of the mean Hartree potential. Using (31) to eliminate $\overline{\Delta E}(n_0^{(0)})$ from (30) we obtain

$$\Delta E = \Delta E_{\text{es}} + \overline{\Delta E}(n_0(0)) - \int d\vec{r}\,\phi_Z^{(0)}(\vec{r})[n_0^{(1)}(\vec{r}) + n_0^{(2)}(\vec{r}) + \cdots - n_0^{(1)}(0) - n_0^{(2)}(0)]$$
$$-\tfrac{1}{2}\int d\vec{r}\left(\phi_Z^{(1)}(\vec{r})n_0^{(1)}(\vec{r}) - \frac{d\phi_Z^{(0)}(\vec{r})}{d\overline{n}}n_0^{(1)}(0)^2\right) + \tfrac{1}{2}\int d\vec{r}\,\phi_Z^{(1)}(\vec{r})[\delta n_0^{+}(\vec{r}) - n_0^{(1)}(\vec{r})] . \tag{32}$$

If the host density is slowly varying on the scale of the quasiatom, only the second term in (32) survives and we recover the uniform-density approximation for the energy that was proposed and tested earlier. The usefulness of (32) is that it provides a method for systematically improving the UDA. It is apparent that the corrections consist of two contributions which are physically distinct. The first is the electrostatic interaction $\Delta E_{\text{es}}$ defined in (29) which we argue should be treated in a nonperturbative fashion because of the nonlocal character of the interactions. The remaining terms in (32) comprise corrections to the quasiatom self-energy itself and arise as a result of variations in the host density over the finite extent of the quasiatom. Since the screening cloud is fairly compact and rigid it is reasonable to expect that this component of the energy is influenced mostly by the local environment. Indeed the form of the terms in (32) suggests an expansion in gradients of the host density which we shall now develop. An alternative approach is based on the observation that the host density in (30) is sampled through the quasiatom Hartree potential and this approach will also be explored.

### A. Gradient corrections

Density gradient corrections have frequently been used to extend local density approximations. The von Weizsäcker correction to the kinetic energy density used in Thomas-Fermi theory and the gradient corrections to the exchange-correlation energy of an inhomogeneous electron gas are well known examples.[2,40] Similar corrections to the quasiatom energy can be developed when the host density is weakly inhomogeneous.

We begin by considering the leading corrections to the quasiatom self-energy which, because of the spherical symmetry of the system, are second order in the density gradient. The quasiatom energy (4) will have the form

$$\Delta E = \Delta E_{\mathrm{es}} + \Delta E_{\mathrm{self}} \tag{33}$$

with

$$\Delta E_{\mathrm{self}} = \overline{\Delta E}(n_0(0)) + a(n_0(0))\,|\nabla n_0|^2 + b(n_0(0))\nabla^2 n_0, \tag{34}$$

where the gradients are evaluated at the position of the impurity. Both kinds of gradient terms must appear, since we are not dealing with an energy density. The coefficients $a(n)$ and $b(n)$ are of course specific for a given impurity. The $a(n)$ term is of the von Weizsäcker form and accounts for a linear spatial variation of the host density; the last term in (34) accounts for a local curvature.

Explicit expressions for the coefficients can be obtained by expanding the host density about the position of the impurity in a Taylor series,

$$n_0^{(1)}(\vec{r}) = n_0^{(1)}(0) + \sum_i r_i \nabla_i n_0^{(1)}(0) + \tfrac{1}{2}\sum_{ij} r_i r_j \nabla_i \nabla_j n_0^{(1)}(0) + \cdots \tag{35}$$

and substituting the result in the right-hand side of (32). For example, the third term in (32) becomes

$$-\int d\vec{r}\,\phi_Z^{(0)}(\vec{r})[n_0^{(1)}(\vec{r}) - n_0^{(1)}(0)] = -\tfrac{1}{6}\nabla^2 n_0^{(1)}(0)\int d\vec{r}\,r^2\phi_Z^{(0)}(\vec{r}) + O(\nabla^4) \tag{36}$$

with a similar result for the part involving $n_0^{(2)}(\vec{r})$.

The reduction of the fourth term in (32) is facilitated by considering the linear response of the quasiatom Hartree potential to an arbitrary change in the host positive charge density

$$\phi_Z^{(1)}(\vec{r}) = \int d\vec{r}'\,K_Z(\vec{r},\vec{r}')\,\delta n_0^{+}(\vec{r}')\ . \tag{37}$$

Here the kernel is given by

$$K_Z(\vec{r},\vec{r}') = -\int d\vec{r}_1 \int d\vec{r}_2 \frac{1}{|\vec{r}-\vec{r}_1|} \times [\chi_Z(\vec{r}_1,\vec{r}_2) - \chi_0(\vec{r}_1-\vec{r}_2)] \times \frac{1}{|\vec{r}_2-\vec{r}'|}\ , \tag{38}$$

where $\chi_Z$ and $\chi_0$ are the density response functions for the impurity and host systems, respectively. The minus sign is simply conventional. $K_Z(\vec{r},\vec{r}')$ is a symmetric function of its arguments, and because of the spherical symmetry of the impurity in jellium system it depends only on the variables $r, r'$ and $\hat{r}\cdot\hat{r}$.

We note that the Fourier transform of the induced host density $n_0^{(1)}(\vec{q})$ is related to that of the perturbation $\delta n_0^{+}(\vec{q})$ by

$$n_0^{(1)}(\vec{q}) = -(4\pi/q^2)\chi_0(\vec{q})\,\delta n_0^{+}(\vec{q})\ . \tag{39}$$

Since the response function $\chi_0$ has the small-$q$ expansion

$$\chi_0(\vec{q}) = -(q^2/4\pi)(1 - c_2 q^2 + \cdots)\ , \tag{40}$$

(39) becomes

$$n_0^{(1)}(\vec{q}) = (1 - c_2 q^2 + \cdots)\,\delta n_0^{+}(\vec{q})\ . \tag{41}$$

The difference between $n_0^{(1)}(\vec{q})$ and $\delta n_0^{+}(\vec{q})$ is of order $q^2$ because of the perfect screening of electrostatic fields at long wavelengths. $\delta n_0^{+}(\vec{r})$ can therefore be expressed in terms of $n_0^{(1)}(\vec{r})$ as

$$\delta n_0^{+}(\vec{r}) = n_0^{(1)}(\vec{r}) - c_2\nabla^2 n_0^{(1)}(\vec{r}) + O(\nabla^4)\ . \tag{42}$$

To the lowest order in gradients considered below, it is permissible to replace $\delta n_0^{+}(\vec{r})$ in (37) by the result (42).

Using the Taylor-series expansion (35) in (37) we obtain

$$\phi_Z^{(1)}(\vec{r}) = \Phi_0(\vec{r})[n_0^{(1)}(0) - c_2 \nabla^2 n_0^{(1)}(0)] + \sum_i \Phi_i(\vec{r}) \nabla_i n_0^{(1)}(0)$$
$$+ \tfrac{1}{2} \sum_{ij} \Phi_{ij}(\vec{r}) \nabla_i \nabla_j n_0^{(1)}(0) + \cdots , \qquad (43)$$

where the expansion functions $\Phi_{ij\ldots}$ are defined by

$$\Phi_{ij\ldots}(\vec{r}) = \int d\vec{r}\,' \, r_i' \, r_j' \cdots K_Z(\vec{r}, \vec{r}\,') \,. \qquad (44)$$

It is apparent that

$$\Phi_0(\vec{r}) = \frac{d\phi_Z^{(0)}(\vec{r};\bar{n})}{d\bar{n}} \quad . \qquad (45)$$

Using (35), (43), and (45) in the fourth term of (32) we find

$$-\tfrac{1}{2} \int d\vec{r} \left( \phi_Z^{(1)}(\vec{r}) n_0^{(1)}(\vec{r}) - \frac{d\phi_Z^{(0)}(\vec{r})}{d\bar{n}} n_0^{(1)}(0)^2 \right)$$
$$= -\tfrac{1}{6} n_0^{(1)}(0) \nabla^2 n_0^{(1)}(0) \int d\vec{r}\, r^2 \frac{d\phi_Z^{(0)}(\vec{r})}{d\bar{n}}$$
$$- \tfrac{1}{6} |\nabla n_0^{(1)}(0)|^2 \int d\vec{r} \sum_i r_i \Phi_i(\vec{r})$$
$$+ \tfrac{1}{2} c_2 n_0^{(1)}(0) \nabla^2 n_0^{(1)}(0) \frac{d\bar{\phi}_Z^{(0)}(\bar{n})}{d\bar{n}} + \cdots , \qquad (46)$$

where the ellipsis represents higher-order gradients and we have used the identity

$$\int d\vec{r}\, r^2 \Phi_0(\vec{r}) = \int d\vec{r} \sum_i \Phi_{ii}(\vec{r}) \qquad (47)$$

to simplify the result. It is clear that the first term in (46) together with (36) is equivalent to

$$- \tfrac{1}{6} \nabla^2 n_0^{(1)}(0) \int d\vec{r}\, r^2 \phi_Z^{(0)}(\vec{r}; n_0(0)) , \qquad (48)$$

where now the *total* host density appears as the argument of the Hartree potential.

Similarly, the last term in (32) becomes

$$- \tfrac{1}{2} c_2 n_0^{(1)}(0) \nabla^2 n_0^{(1)}(0) \frac{d\bar{\phi}_Z^{(0)}(\bar{n})}{d\bar{n}} \quad , \qquad (49)$$

which cancels with the last term in (46). Thus we conclude that the quasiatom self-energy indeed has the form shown in (34) with the coefficients given by [see (46) and (48)]

$$a(n) = - \tfrac{1}{6} \int d\vec{r} \sum_i r_i \Phi_i(\vec{r}; n) \qquad (50)$$

and

$$b(n) = - \tfrac{1}{6} \int d\vec{r}\, r^2 \phi_Z^{(0)}(\vec{r}; n) \,. \qquad (51)$$

The fact that the final result is as simple as it is attests to the correctness of dividing the quasiatom energy into the electrostatic and self-energy parts.

The coefficient $b(n)$ is determined by the Hartree potential of the quasiatom and has been evaluated for He in the metallic density range. The results are fairly constant for densities between 0 and 0.05 a.u. being fitted to within 2% by the polynomial $b^{\mathrm{He}}(n) = 4.3 - 300\, n^2$ a.u. The calculations were not actually performed using (51) because of the slow asymptotic decay of the potential $\phi_Z(\vec{r}) \sim \cos(2k_F r + \phi)/r^3$, although the insertion of a damping factor in the integrand can avoid this difficulty. Instead it was found more convenient to work with the Fourier transform of $\phi_Z(\vec{r})$, $\tilde{\phi}_Z(\vec{q})$, in terms of which $b(n) = \frac{1}{6}[\nabla_{\vec{q}}^2 \tilde{\phi}_Z(\vec{q})]_{\vec{q}=0}$. Even so there is some uncertainty in the results, particularly at low density where the error could be as large as 10%.

The coefficient $a(n)$ is more difficult to evaluate since it involves explicit knowledge of the kernel $K_Z(\vec{r}, \vec{r}\,')$ or equivalently, the density response function $\chi_Z(\vec{r}, \vec{r}\,')$ of the impurity-jellium system. We shall therefore limit ourselves to some general comments concerning the physical interpretation of the correction with which it is associated and a possible method for its evaluation.

As can be seen from (37) and (44) the function $\Phi_i(\vec{r})$ appearing in (50) describes the response of the quasiatom to a linear density variation which effectively acts as an external electric field. The first moment of this response (50) is thus analogous to the dipole polarizability of an atom. Some indication of the importance of the $a(n)$ correction can be inferred from the ease with which the free atom is polarized. However, a quantitative estimate based on the free-atom polarizability cannot be made since the electron gas has a considerable influence on the response of the quasiatom. The polarizability depends sensitively on the valence-electron states which in the case of the quasiatom consist of the continuum states that contribute to the Friedel oscillations around the impurity. As demonstrated by the mean Hartree potential, these oscillations can have an important effect on the quasiatom properties. In the case of H at low densities the screening cloud resembles an $H^-$ ion and obviously will respond differently from the neutral atom. A second effect is that the induced dipole moment of the quasiatom will itself give rise to fields to which the surrounding electron gas responds. A self-consistent solution of this problem is clearly indicated.

Some supplementary information can be obtained from (45), (44), and (19) which imply

$$\frac{d^2\overline{\Delta E}}{d\bar{n}^2} = - \int d\vec{r} \int d\vec{r}\,' K_Z(\vec{r}, \vec{r}\,') \,. \qquad (52)$$

Since the dimensions of the quasiatom are of the order of a Bohr radius, we might expect $a(n) \sim d^2\overline{\Delta E}/d\bar{n}^2$. Based on this estimate the coefficient $a(n)$ should be small for He and for H in a spin-polarized host at all metallic densities but may be significant for H in a paramagnetic gas having a density near the minimum of the energy curve (Fig. 4). This latter situation arises when H is near a metal surface and may account for the discrepancy observed in the UDA chemisorption energies.

A direct calculation of the coefficient $a(n)$ is straightforward in principle. The induced change in the screening cloud $\Delta n_Z^{(1)}$ which can be calculated with the response function $\chi_Z(\vec{r}, \vec{r}\,')$ is required when a small density gradient is superimposed on the jellium. With the atom at the origin a perturbing positive charge distribution $\delta n_0^+(\vec{r}) = \lambda \sin\vec{Q}\cdot\vec{r}$ will produce the desired effect. Within the Kohn-Sham method the response of the quasiatom to a perturbation of this sort is determined by a linear integral equation which involves the independent particle density response function for the atom in jellium. The methods applied by the authors in their study of free-atom polarizabilities[41] can also be used in this case to obtain a tractable form for the response function and the integral equation but details of the theory and results will be presented elsewhere.

Before closing this subsection we return to a discussion of the electrostatic energy $\Delta E_{\text{es}}$. In the expanded form shown in (29) it is apparent that $\Delta E_{\text{es}}$ will tend to cancel the third term in (32) which also contains a first-order contribution. This cancellation will be evident in later applications and partly explains the success of the UDA. With (43) we can write

$$\Delta E_{\text{es}} = \int d\vec{r}\,[n_0(\vec{r}) - n_0^+(\vec{r})]\left(\phi_Z^{(0)}(\vec{r};\bar{n}) + \frac{d\phi_Z^{(0)}(\vec{r};\bar{n})}{d\bar{n}}\, n_0^{(1)}(0) + \sum_i \Phi_i(\vec{r})\nabla_i n_0^{(1)}(0) + \tfrac{1}{2}\sum_{ij} \Phi_{ij}(\vec{r})\nabla_i\nabla_j n_0^{(1)}(0) - c_2\,\frac{d\phi_Z^{(0)}(\vec{r};\bar{n})}{d\bar{n}}\,\nabla^2 n_0^{(1)}(0) + \cdots\right). \tag{53}$$

Here we have left the host density in a nonperturbative form but expanded the quasiatom potential $\phi_Z(\vec{r})$ in gradients. When written in this form it is clear that the quasiatom density is being developed in a multipole expansion, each multipole interacting electrostatically with the host charge density. The first two potential terms combine to give $\phi_Z^{(0)}(\vec{r};n_0(0))$, again indicating that the local host density is relevant in defining the quasiatom. As a first approximation to $\Delta E_{\text{es}}$ the $\phi_Z^{(0)}(\vec{r};n_0(0))$ term can be used, while the gradient terms can be added if refinements to this value are desired.

### B. The sampled local density

A different approach from that of density gradient corrections has been suggested to extend the local density approximation for electron exchange and correlation energy.[42,43] Gunnarsson *et al.*[42] have emphasized that an electron at position $\vec{r}$ samples the electron density over a region the size of its exchange-correlation hole. The exchange-correlation energy density is then obtained by using the energy of a uniform electron gas having a density equal to an appropriately sampled local density. This refinement improves the exchange energy of light atoms. In the same spirit we propose a sampling technique suggested by the form of the perturbation expansion (30) which weights the local host density by the quasiatom Hartree potential. Specifically we define a sampled host density $\bar{n}_0(0)$ through

$$\bar{n}_0(0)\int d\vec{r}\,\phi_Z(\vec{r}) \equiv \int d\vec{r}\, n_0(\vec{r})\phi_Z(\vec{r})\ . \tag{54}$$

With this definition, the second and third terms in (30) can be combined to give

$$\begin{aligned}\overline{\Delta E}(n_0^{(0)}) - \int d\vec{r}\,\phi_Z^{(0)}(\vec{r})[n_0^{(1)}(\vec{r}) + n_0^{(2)}(\vec{r}) + \cdots\,] &= \overline{\Delta E}(n_0^{(0)}) - \bar{\phi}_Z^{(0)}[\bar{n}_0(0) - n_0^{(0)}] \\ &= \overline{\Delta E}(n_0^{(0)}) + \frac{d\overline{\Delta E}}{d\bar{n}}[\bar{n}_0(0) - n_0^{(0)}] \\ &\simeq \overline{\Delta E}(\bar{n}_0(0)),\end{aligned} \tag{55}$$

where we have again used the slope theorem (18). This result suggests the *ansatz* for the quasiatom energy

$$\Delta E \simeq \Delta E_{\text{es}} + \overline{\Delta E}(\bar{n}_0(0)) \tag{56}$$

which accounts for inhomogeneities in the host through the sampled density. Here $\Delta E_{\text{es}}$ is the electrostatic energy (29), which can be approximated as described before. If $\phi_Z(\vec{r})$ in (54) is chosen to be $\phi_Z^{(0)}(\vec{r};n_0(0))$, i.e., the Hartree potential in jellium, information about the gradient in the local density is lost and therefore the ansatz cannot account for terms such as the second in (34). We would therefore expect this sampling to work best when only a curvature in the local host density is present. A further shortcoming of the $\phi_Z^{(0)}(\vec{r};n_0(0))$ weighting is that the sampled density becomes indeterminate when $\bar{\phi}_Z^{(0)}=0$, i.e., for $n_0(0)$ at the minimum of the energy curve. An improved sampling technique which would account for distortions of the screening cloud could perhaps be the use of the additional terms in (43) to define the weighting function in (54).

The sampling technique is closely related to the gradient expansion (34). For example, if the host density is slowly varying, (54) gives

$$\bar{n}_0(0)\simeq n_0(0)+\tfrac{1}{6}\nabla^2 n_0(0)\,\frac{\int d\vec{r}\,r^2\phi_Z^{(0)}(\vec{r})}{\int d\vec{r}\,\phi_Z^{(0)}(\vec{r})}\;. \tag{57}$$

In the case that the correction to $n_0(0)$ is small we have

$$\overline{\Delta E}\,(\bar{n}_0(0))\simeq\overline{\Delta E}(n_0(0)) - \tfrac{1}{6}\nabla^2 n_0(0)\int d\vec{r}\,r^2\phi_Z^{(0)}(\vec{r};n_0(0)), \tag{58}$$

which reproduces the gradient expansion. However, if $[\bar{n}_0(0)-n_0(0)]$ is not small and if $n_0(\vec{r})$ is not slowly varying, the sampling ansatz includes an infinite summation of terms going beyond second order in gradients. In this sense the sampling ansatz can be regarded as an approximate extension of the rigorous gradient expansion.

### C. Tests of corrections to the UDA

Further calculations for the simple model situation of an He atom in a vacancy in jellium have been performed to test the validity of the corrections discussed in the previous sections. The binding energy of the atom to the vacancy has been calculated using both the gradient expansion (33) and the sampling ansatz (56) for the quasiatom energy. Since there is no gradient in the host density at the center of the vacancy, only the curvature correction contributes to the energy.

Results for $\Delta E_{\rm es}$ are given in Table I. These were calculated using the first term in (53) with the quasiatom potential evaluated at the local density (the density at the center of the vacancy). The electrostatic energies are all negative due to the strongly attractive $\phi_Z(\vec{r})$ for $r_s \lesssim 3$ a.u. As the mean host density decreases or as the valence of the vacancy increases, the density at the center of the vacancy decreases and the energy $\Delta E_{\rm es}$ becomes progressively smaller in magnitude. As a check on the approximation used, the electrostatic energy has been calculated exactly for one case by explicitly subtracting $n_Z(\vec{r})$ and $n_0(\vec{r})$ to obtain the screening charge for He in the vacancy and hence $\phi_Z(\vec{r})$. This result is shown in parentheses in Table I and the excellent agreement with the approximate result indicates the validity of the uniform-density approximation for $\phi_Z(\vec{r})$. It would be of interest to check this for more reactive atoms such as H.

The curvature corrections, $b(n_0(0))\nabla^2 n_0(0)$, have also been evaluated; their variation with mean density and $Z_v$ is mainly due to the variation of the density curvature in the vacancy since the coefficient $b(n)$ depends little on $n$. The effect of the curvature corrections is to increase the effective host density sampled by the atom and therefore increase the self-energy because of the positive slope of the energy curve for He. The curvature correction cancels some of the electrostatic energy which is likely to be a general feature. However, all the terms in the approximate treatment are of the order of magnitude of the final binding energy and the cancellation is not excessive as in conventional perturbation treatments using pseudopotentials.

The total He-vacancy binding energies calculated according to (33) are listed in Table I and are in excellent agreement with the exact results which are also shown.

Sampled host densities for He in a jellium vacancy have been calculated according to (54) with $\phi_Z(\vec{r})$ evaluated at $n_0(0)$ and the results are given in Table I. The sampled densities are all greater than the local density at the center of the vacancy due to the positive curvature of the density. The effect on the impurity energy of using a sampled rather than the local host density is the same as that of the curvature corrections. The He-vacancy binding energies calculated according to (56) are listed in the table and the agreement with the exact results is again excellent. In these cases the sampling technique yields slightly superior results to the gradient expansion. The corrected binding energies are also plotted on Fig. 3 and the general improvement over the UDA is evident.

The sampling ansatz (56) has also been adopted recently by Nørskov and Lang[13] in the calculation of chemisorption energies for H and O on jellium surfaces. Although only the electrostatic correction $\Delta E_{\rm es}$ was included, substantial improvements over the UDA were reported, which seems to indicate that the gradient corrections are small in the cases they considered.

## VI. CONCLUSIONS

We have demonstrated that the uniform-density approximation for the quasiatom energy works well in a variety of situations. Qualitative trends are reproduced for both H and He, atoms which are chemically very different. Impurity energies are given typically to about 1 eV or better in the metallic situations (vacancy-impurity binding, chemisorption), however, larger discrepancies are found for the hydrogen molecules. The most serious shortcoming occurs when the atom is separated from the host system and is manifested in the diatomic metal hydrides and chemisorbed H through the incorrect dissociation products.

Considering the degree of nonuniformities in the hosts that have been studied, the success of the UDA is perhaps unexpected. An extreme example is the case of the $^3\Sigma_u^+$ state of $H_2$ in which the electron density of the host H atom varies by approximately a factor of 10 over the extent of the quasiatom. The validity of the approximation appears to involve more than just the assumption of a slowly varying host density and the situation is reminiscent of the local density approximation for electron exchange and correlation. The latter, which has proven to be very successful even in cases where the electron density is rapidly varying, has been explained from various points of view.[44, 22] The similar success of the quasiatom picture in the UDA implies that the nonuniformities in the host density are being averaged in a realistic way and some support for this conclusion is provided by the gradient expansion. More generally it appears that a slowly varying host density is a sufficient but not a necessary requirement for the application of the UDA.

The quasiatom energy curves contain all the information necessary for an application of the UDA. Judging from the examples we have studied, it seems likely that the energy curves will fall into two main categories. Atoms which are chemically inert should have linear energy curves whereas reactive elements, particularly those with stable negative ions, will tend to show a minimum at low densities followed by a linear increase at higher densities. The main parameters of the curves are the position and depth of the minimum and the slope of the linear portion at higher densities. The latter can be used to define the effective number of electrons which are sensitive to the environment of the atom through $Z_{\text{eff}}\, d\bar{\mu}/d\bar{n} \equiv d\overline{\Delta E}/d\bar{n}$, i.e., an effective valence. For the moment this is a purely suggestive procedure and more work is necessary to see in detail how this and the other parameters might correlate with the atom's position in the Periodic Table.

The Wigner lattice model seems to provide a simple explanation of a minimum in the energy curve in terms of the tendency to form a negative ion. It would predict a minimum for the halogens similar to that of hydrogen, while in the case of oxygen, a deeper minimum would be expected because $O^{2-}$ would form in some range of densities. This latter situation has been verified in recent calculations of Nørskov and Lang.[13]

Corrections to the UDA have also been investigated. As indicated by the general expression, Eq. (4), the quasiatom energy consists of an electrostatic interaction with the unperturbed host and a self-energy part which is influenced by local host nonuniformities. Both of these parts contribute in the correction to the UDA as defined either in the form of a gradient expansion or by the alternative sampling ansatz. As seen in the calculation of the He-vacancy binding energy, both kinds of corrections were needed to achieve the good agreement shown in Table I. More importantly, this test demonstrates the feasibility of correcting the UDA by either the gradient expansion or the sampling technique. The former is perhaps to be preferred because of the possible problems that can arise with the sampling ansatz [see Sec. V(B)]. Although gradient corrections to the LDA for inhomogeneous electron gas problems have not proved successful,[45] they may be more useful in correcting the UDA because of the compact and rigid nature of the quasiatom.

The response of the quasiatom to a gradient in the host density is likely to be correlated with the curvature in the energy curve. Thus the gradient correction $a(n)$ is probably small for He but significant for reactive atoms, particularly in situations close to the minimum in their energy curves. A method for calculating the $a(n)$ coefficient was outlined in Sec. V A, and it is to be hoped that detailed calculations in a few cases will reveal correlations between the quasiatom response and free-atom properties such as the dipole polarizability. An application of the gradient correction $a(n)$ to the chemisorption problem would be of considerable interest.

The quasiatom approach for estimating impurity energies in real systems requires knowledge of the host electron density. Unless this density can be obtained in a relatively straightforward way many of the advantages of the approach cannot be realized. Fortunately, the host density can be estimated to sufficient accuracy in various solid-state problems of interest. For the example of impurity diffusion in solids the perfect-crystal density is required which ideally would be obtained from a band-structure calculation. The simplification of the quasiatom approach is immediately apparent in this case since various well-documented methods for dealing with the perfect host have been developed while the impurity problem is almost intractable. However, even a simple superposition approximation for the density may be adequate; with

$$n_0(\vec{r})=\sum_i n_a(\vec{r}-\vec{R}_i)\ ,$$

$n_a$ can be chosen to be the free-atom charge density for transition-metal hosts, whereas for simple metals neutral pseudoatoms[46] should suffice. Another possibility is to consider the host atom in its jellium vacancy and using the displaced electron density in this situation as the ingredient for the superposition approximation. A useful application of this scheme would be a study of hydrogen solution and the diffusion of light impurities such as muons and protons in metals for which the impurity potential is required. A cautionary word is in order, however, since it is not clear at present what contribution to the sampled density or the eldctrostatic interaction $\Delta E_{es}$ will arise from the ion core regions of host atoms near the impurity where electron densities and electrostatic potentials are very large. Exact quasiatom electron densities and Hartree potentials may differ significantly from the jellium results due to orthogonality and more work is needed to see if this creates difficulties.

Finally we should mention some other work which is related to ours in the sense that the local properties of the impurity are emphasized. The neutral pseudoatom of Ziman[46] can be viewed as an approximation to the quasiatom described here in which the impurity is represented by a weakly scattering pseudoion and the screening cloud is calculated to first order in perturbation theory. Generalizations to strong potentials have also been developed, particularly by Ball.[47] In the latter work the impurity potential is calculated self-consistently in much the same way as is done here and various alloy properties can be accounted for successfully in terms of the impurity scattering phase shifts. However, the concept of a quasiatom is seen to be more generally applicable and is especially suited to obtaining a quantitative estimate of the impurity energy.

## ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada. We are grateful to J. K. Nørskov and N. D. Lang for the communication of results and a copy of their manuscript prior to publication. We would like to thank W. M. Sribney for help with the numerical work. One of us (M. J. S.) acknowledges discussions with C. H. Hodges and J. E. Inglesfield and the hospitality of the Daresbury S. R. C. Laboratory, England where some of this work was performed.

---

[1] J. C. Slater, *Quantum Theory of Matter*, 2nd ed. (McGraw-Hill, New York, 1968).

[2] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[3] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[4] M. Hamazaki, S. Asano, and J. Yamashita, J. Phys. Soc. Jpn. 41, 378 (1976); R. Zeller and P. H. Dederichs, Phys. Rev. Lett. 42, 1713 (1979).

[5] N. D. Lang and A. R. Williams, Phys. Rev. Lett. 34, 531 (1975); *ibid.* 37, 212 (1976); O. Gunnarsson, H. Hjelmberg, and B. I. Lundqvist, Surf. Sci. 63, 348 (1977); H. Hjelmberg, O. Gunnarsson, and B. I. Lundqvist, *ibid.* 68, 158 (1977).

[6] H. Hjelmberg, Phys. Scr. 18, 481 (1978).

[7] B. I. Lundqvist, J. K. Nørskov, and H. Hjelmberg, Surf. Sci. 80, 441 (1979).

[8] T. B. Grimley and C. Pisani, J. Phys. C 7, 2831 (1974); J. Keller, in *Computational Methods for Molecules and Localized States in Solids*, edited by F. Herman, A. D. McLean, and R. K. Nesbet (Plenum, New York, 1973), p. 341; J. E. Inglesfield, J. Phys. F 9, 1551 (1979).

[9] R. P. Messmer and D. R. Salahub, Phys. Rev. B 16, 3415 (1977), and references therein.

[10] V. Heine and D. Weaire, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 249.

[11] M. J. Stott and E. Zaremba, Solid State Commun. 32, 1297 (1979).

[12] D. S. Larsen and J. K. Nørskov, J. Phys. F (in press).

[13] J. K. Nørskov and N. D. Lang, Phys. Rev. B 21, 2131 (1980).

[14] Z. D. Popović and M. J. Stott, Phys. Rev. Lett. 33, 1164 (1974); C.-O. Almbladh, U. von Barth, Z. D. Popović, and M. J. Stott, Phys. Rev. B 14, 2250 (1976); E. Zaremba, L. M. Sander, H. B. Shore, and J. H. Rose, J. Phys. F 7, 1763 (1977).

[15] M. D. Whitmore, J. Phys. F 6, 1259 (1976).

[16] J. K. Nørskov, Solid State Commun. 24, 691 (1977).

[17] M. Manninen, P. Hautojärvi, and R. Nieminen, Solid State Commun. 23, 795 (1977).

[18] U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).

[19] P. Jena, K. S. Singwi, and R. M. Nieminen, Phys. Rev. B 17, 301 (1978) as corrected in R. M. Nieminen and M. Manninen, Hyp. Int. 6, 25 (1979); R. L. Munjal and K. G. Petzinger, *ibid.* 4, 301 (1978).

[20] H. F. Budd and J. Vannimenus, Phys. Rev. Lett. 31, 1218 (1973); J. Vannimenus and H. F. Budd, Solid State Commun. 15, 1739 (1974).

[21] M. Manninen, R. Nieminen, P. Hautojärvi, and J. Arponen, Phys. Rev. B 12, 4012 (1975).

[22] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).

[23] However, it should be noted that in the limit of high mean densities $\bar{\phi}_Z$ tends to zero as $r_s$ and so the energy curve will eventually flatten.

[24] B. Y. Tong and L. J. Sham, Phys. Rev. 144, 1 (1966).

[25] H. D. Cohen, J. Chem. Phys. 43, 3558 (1965).

[26] Reasonable limiting procedures for evaluating the ill-defined integral in (20) yield the same result as obtained from the convergent integral in (18).

[27] H. B. Shore, J. H. Rose, and E. Zaremba, Phys. Rev. B 15, 2858 (1977).

[28] K. Schwartz, Chem. Phys. Lett. 57, 605 (1978); J. Phys. B 11, 1339 (1978).

[29] N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).

[30] O. Gunnarson, B. I. Lundqvist, and J. W. Wilkins, Phys. Rev. B 10, 1319 (1974).

[31] N. D. Lang and W. Kohn, Phys. Rev. B 3, 1215 (1971).

[32] C. L. Pekeris, Phys. Rev. 126, 1470 (1962).

[33] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1963).

[34] K. P. Huber, in *American Institute of Physics Handbook*, edited by D. E. Gray, 3rd ed. (McGraw-Hill, New York, 1972), p. 7.168.

[35] W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. 32, 219 (1960).

[36] C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976).

[37] For Thomas-Fermi atoms $\bar{\phi}_Z$ scales as $Z^{1/3}$.

[38] L. M. Kahn and S. C. Ying, Surf. Sci. 59, 333 (1976).

[39] R. Feder, Phys. Rev. B 2, 828 (1970).

[40] D. J. W. Geldart and M. Rasolt, Phys. Rev. B 13, 1477 (1976), and references therein.

[41] M. J. Stott and E. Zaremba, Phys. Rev. A 21, 12 (1980).

[42] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Lett. 59A, 177 (1976); Solid State Commun. 24, 765 (1977); Phys. Rev. B 20, 3136 (1979).

[43] J. A. Alonso and L. A. Girifalco, Phys. Rev. B 17, 3735 (1978).

[44] J. Harris and R. O. Jones, J. Phys. F 4, 1170 (1974); E. Wikborg and J. E. Inglesfield, Solid State Commun. 16, 335 (1975); N. D. Lang and L. J. Sham, *ibid.* 17, 581 (1975); G. D. Mahan, Phys. Rev. B 12, 5585 (1975).

[45] J. P. Perdew, D. C. Langreth, and V. Sahni, Phys. Rev. Lett. 38, 1030 (1977).

[46] J. M. Ziman, Adv. Phys. 13, 89 (1964).

[47] M. A. Ball and M. S. Farthing, J. Phys. F 9, 1223 (1979).