Simple model of hydrogen and lithium chemisorption on jellium substrates

J. P. Muscat and D. M. Newns

Department of Mathematics, Imperial College, London S.W.7., England

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Within a simple one-parameter quasianalytic model, we are able to reproduce the main one-body features of first-principles calculations for hydrogen chemisorption on jellium surfaces. These include the qualitative variation in the width and position of the resonance peaks as the adatom-substrate separation is allowed to change. The general variation of these features with the elctron density of the substrate is also reproduced with remarkable accuracy. Preliminary results for Li adsorption are also presented, and also seem to be compatible with the limited data from first-principles calculations. Nevertheless the limitation of the present model to an l = 0 solution means that it cannot include *sp*-hybridization effects which appear to be important. The simplicity of the current model enables a simple physical interpretation of the mechanism of chemisorption on free-electron-like substrates. In addition there is a strong possibility of extension of our model to systems, of greater practical importance, for which a first-principles calculation is as yet not possible.

I. INTRODUCTION

This paper has arisen from the need to understand, and to place in the context of the whole theory of chemisorption, a series of important recent first-principles calculations for chemisorption on free-electron-like substrates.¹⁻⁵ These calculations employ the remarkably successful local-density-functional (LDF) approach;⁶ we remind ourselves that this approach seems to give an excellent approximation to the ground state of various systems, its application to the excitation spectrum being, however, rather less firmly based. Furthermore, the approach is formally similar to the Hartree theory, it being the case that once the self-consistent Hartree-like potential is established, solving for the wave functions and energy levels is only a one-body problem.

The calculations in question¹⁻⁵ all uniformly employ as a starting point the jellium model, in which the substrate ion-core charge density is smeared out to form a uniform positive background truncated stepwise at the surface. This model is often considered as a useful starting point for considering the surface properties of the clean sp-metal surfaces.⁷ In the chemisorption calculations a point charge, of magnitude equal to that of the nucleus of the adatom in question, is added to the jellium background at a distance d from the "jellium edge," at which the background drops to zero. The major numerical task of re-solving the LDF equations is then undertaken. The chemisorption energy, the dipole moment, and the change in density of states $\Delta N(\epsilon)$ on adsorption are among the quantities calculated. Calculations exist for H, O, Li, Cl, and Si adsorbates on jellium done in this way.1-3 Calculations have also been made for H and O adsorbates in which the substrate atomic structure is taken

into account using a perturbational calculation to first order in the substrate ion-core pseudopotentials.³⁻⁵ The substrate pseudopotentials are found to modify radically such properties as the equilibrium distance d (and hence the nature of substrate-adsorbate binding); the chemisorption energy and dipole moment being also modified. However, $\Delta N(\epsilon)$ at a given d is not usually corrected for the pseudopotentials, and we shall similarly ignore this effect in the following. It is, however, possible to take into account the substrate pseudopotentials in a nonperturbational way by means of a cluster calculation, as done by Harris and Painter,⁸ for example.

A word should be said on the experimental importance of sp metals as substrates in chemisorption, for which less well-established highquality experimental information appears to be available than for transition metal or semiconductor substrates. For example, on exposure of aluminum to oxygen there remains uncertainty as to whether adsorption or absorption of the oxygen takes place.4,9 The chemisorption of hydrogen on such metals as Al, Mg, and the alkalis seems not to have been established.¹⁰ On the other hand, hydrogen should chemisorb (if it is not absorbed) on the latter systems in its atomic state.¹⁰ Such an adsorbed layer is stable with respect to desorption if the atomic chemisorption energy ΔE exceeds half the H₂ dissociation energy, i.e., exceeds 2.3 eV.¹¹ For, say, Al low-index faces, the above-mentioned calculations suggest ΔE is insufficient for such stability,^{1,3,5} but, nevertheless, at sufficiently low temperatures such that diffusion is negligible the adsorbed H atoms should be observable in a metastable state as found for H on some noble metals.¹²

In the alkali adsorbates the rather similar properties of various transition metal substrates¹³

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and the large radius of the valence-shell electronic states suggests that the transition metal dbands, specially when narrow, might not be very important in the substrate-adsorbate interaction. In such a case the substrate sp band might be dominant and a free-electron-like model of the substrate — whose d electrons are treated as cores — might be useful in calculating some properties. Lang has rather successfully discussed the work function change in alkali chemisorption on transition metal systems using a jellium model for the substrate.¹³

One aim of the present work, of which short accounts have previously been published,^{14,15} is to aid interpretation and understanding of the jellium-based calculations for hydrogen on freeelectron-like substrates. In chemical terms, we would like to know whether the hydrogen is to be regarded as adsorbed in essentially atomic form, or whether there is a recognizable chemical bond. The former view seems suggested by earlier work within an approximate LDF formalism,¹⁶ where an atomiclike resonance was calculated. In view of the improved treatments now available,¹⁻⁵ which, as we shall show, suggest the contrary view, the results of Ref. 16 will not be further discussed here.

We shall concentrate on the change in density of states $\Delta N(\epsilon)$ on chemisorption, and follow the usual approximation of assuming the main effect of substrate pseudopotentials is to give a more realistic d without changing $\Delta N(\epsilon)$ at that d. We regard this quantity as containing valuable information as to the nature of the chemical bond in the LDF ground state. Its relationship with the actual excitation spectrum is regarded as secondary here. The present work is confined to monovalent adsorbates, mainly hydrogen but lithium is also considered. The approach is to start by trying to identify the main physical elements in the adatom-substrate interaction, which are incorporated into a simple model whose results are then compared with the first principles calculations.

Let us first outline the physical ideas, taking hydrogen as the example. Our starting point is the Anderson model of chemisorption within the restricted Hartree-Fock formalism,^{17,18} This has a number of points in common with LDF formalism. In this picture one starts with a self-consistent effective hydrogen 1s level, ϵ_{eff} , which for a slightly negatively charged adatom lies a little above the mean of the ionization and affinity levels — say at 6 eV below vacuum level. The change in density of states $\Delta N(\epsilon)$ due to bringing up the adatom is then

$$\Delta N(\epsilon) = 2\pi^{-1} \frac{d\eta(\epsilon)}{d\epsilon}, \qquad (1a)$$

where the phase shift $\eta(\epsilon)$ is given by¹⁹

$$\eta(\epsilon) = -\tan^{-1} \left\{ \Delta(\epsilon) / [\epsilon - \epsilon_{eff} - \Delta(\epsilon)] \right\};$$

 $0 < \eta < \pi$. (1b)

The function $\Delta(\epsilon)$, central to the theory, is defined by

$$\Delta(\epsilon) = \sum_{k} |\langle 1s | V | k \rangle|^2 \delta(\epsilon - \epsilon_k), \qquad (2)$$

where $|k\rangle$ is a band state of the semi-infinite metal with energy ϵ_k and $|1s\rangle$ is the H valence orbital, V being the perturbation on bringing the atom up to the surface.¹⁸ $\Lambda(\epsilon)$ is the Hilbert transform of $\Delta(\epsilon)$.

It is seen from Eq. (1) that if Δ is small there is a sharp peak or resonance in ΔN which occurs at an energy ϵ_1 , given by the solution of the transcendental equation

$$\epsilon - \epsilon_{\text{aff}} - \Lambda(\epsilon) = 0.$$
⁽³⁾

In Fig. 1 we illustrate the graphical solution of (3). $\Delta(\epsilon)$ and $\Lambda(\epsilon)$ have been taken for simplicity to have the form

$$\begin{split} \Delta &= c \left(1 - \epsilon^2\right)^{3/2}, \\ \Lambda &= c \left\{\frac{1}{2} \epsilon \left(3 - 2\epsilon^2\right) + \left[\Theta(\epsilon - 1) - \Theta(-1 - \epsilon)\right] \left(\epsilon^2 - 1\right)^{3/2}\right\}, \end{split}$$



FIG. 1. Anderson model approach. (a) Functions Δ and Λ for c=1 (see Sec. I) with graphical solution of Eq. (3). (b) Quantity $\Delta n(\epsilon)$ plotted vs ϵ at $\epsilon_{\rm eff} = -0.2$ for various values of c; curves labeled by c.

where Θ is the step function and c is a scaling constant. Note the $\epsilon^{3/2}$ behavior of Δ at bottom of band, as would be appropriate for the surface density of states. However, since an upper cutoff is required, we have for simplicity taken a symmetric Δ , though this would be more natural for a tight-binding system. Accordingly, the results obtained from this model will not be very meaningful for a jellium surface in, say, $\epsilon \ge 0.5$. From Fig. 1 it is seen that ϵ_1 lies below ϵ_{eff} . The larger Λ (which scales with Δ), is, the larger this lowering will be; (a) and (b) in Fig. 1 refer, respectively, to small and large Δ . Since the matrix element V_{ak} , and hence Δ , is expected to increase as the atom approaches the surface, it is thus expected that ϵ_1 will drop uniformly below $\epsilon_{\rm eff}$ as the atom approaches the surface; (a) and (b) in Fig. 1 can be regarded as appropriate for large and small atom-surface distance, respectively.

The width of the resonance is $\Delta(\epsilon_1)$. This resonance width is thus expected at first to increase as the atom approaches the surface, but if ϵ_1 gets near the bottom of the band it will decrease again. Finally, if ϵ_1 goes below the band edge [which is actually the case in Fig. 1(b)] ϵ_1 becomes a localized state.

In Fig. 1(b) we also illustrate the phase shift $\eta(\boldsymbol{\epsilon})$ through the proportional quantity $\Delta n(\boldsymbol{\epsilon})$ $=2\eta(\epsilon)/\pi$. $\Delta n(\epsilon)$ is the change in number of electrons bound below energy ϵ due to adding the hydrogen, its derivative being $\Delta N(\epsilon)$ [see Eq. (1a)]. $\epsilon_{\rm eff}$ is chosen to lie near the band center. The curve c = 0.08 corresponds to a line somewhat steeper than case (a) of Fig. 1(a). The shape of $\Delta n(\epsilon)$ is characteristic of a well-defined atomic resonance, showing a rapid change in $\Delta n(\epsilon)$ as one traverses through it, from Δn small at $\epsilon = -0.5$ to Δn nearly 2 at $\epsilon = 0$. In the case c = 2.7 on the other hand, one has a bound state below band and also above it, corresponding to case (b) of Fig. 1(a). In studies of the Anderson model of chemisorption¹⁸ it is well established that these bound states are bonding and antibonding states, respectively. We expect these states together to contribute $\Delta n = 2$ electrons (since one atomic orbital $|a\rangle$ has been added to the system), but each state only $\Delta n \simeq 1$; thus, the value of Δn near midband should correspond to about unity, corresponding to a bonding state. Looking at the c = 2.7curve, we see it has $\Delta n \approx 2$ for ϵ near bottom of the band, as it must due to the bound state, but this value drops rapidly to about 1 at midband in accordance with the above simple argument.

A subtle situation is found at values of c between the atomic and covalent limits. At c = 0.65, an atomiclike resonance, broader than at c = 0.08 is found, but Δn tends to saturate at about 1.2; this resonance is *not* purely atomic but has some bonding character. At c = 1.2 we have again a sharp resonance, just above bottom of band. The resonance itself binds 1.4 electrons, seeming paradoxically more atomiclike than at c = 0.65. However, the resonance gives itself away on looking at $\Delta n(\epsilon)$ for larger ϵ , where a fall-off reminiscent of the bonding state case c = 2.7 is seen, which shows the resonance is really a "virtual bonding state."

To summarize the discussion of the Anderson model, it is expected that there is a narrow atomiclike resonance at $\epsilon_{eff} \sim 6$ eV below vacuum at large d, which broadens and shifts down with decreasing d. If the coupling is strong enough, on further decreasing d, the resonance will narrow on approaching the bottom of the band and may then appear as a bonding state. Consideration of the area $\Delta n(\epsilon)$ under the resonances can further be used as a diagnosis for bonding or atomic character. Furthermore, if ϵ_{eff} and ϵ_F lie near the center of the band, then bonding-type resonances or bound states will be occupied (and antibonding unoccupied) leading to an important contribution to the binding energy from these states.

The change in density of states $\Delta N(\epsilon)$ according to LDF calculations when a proton is introduced at distance *d* from the jellium edge is shown in Fig. 2 for $r_s = 2$ and 3.⁵ Broadly, the features just described are indeed seen. At large *d* there is a narrow level at $\epsilon_{eff} \simeq 6$ eV below vacuum level for $r_s = 2$ and $r_s = 3$ (at $d = \infty$ the level is found to be at 7 eV below vacuum). In both cases this level at first broadens and shifts down with decreasing *d*, then narrows on approaching the bottom of the band. Finally, it is known from calculations done for a proton well inside jellium that when $r_s > 1.9$ there is a bound state just below the bottom of the band.²⁰

An attempt to make a more quantitative application of these ideas, which seem qualitatively correct, encounters difficulties in calculating $\Delta(\epsilon)$. This applies particularly to the high-energy behavior which is essential to get correct if the Hilbert transform $\Lambda(\epsilon)$ is to be calculated.

In the present work, the explicit calculation of $\Delta(\epsilon)$ is avoided by using the Korringa-Kohn-Rostoker (KKR) formalism.²¹ In this method, the potential of the system is approximated by one which is spherically symmetric within a sphere of radius *R* centered on the proton, whereas outside the sphere it is the potential of the unperturbed surface. It is then possible to express $\Delta N(\epsilon)$ in terms of (i) the one-electron Green's function of the unperturbed surface and (ii) the solution of the Schrödinger equation of angular momentum *l*



FIG. 2. Change in density of states $\Delta N(\epsilon)$ due to chemisorption of the H atom on the jellium surface according to first-principles calculations of Ref. 5. Curves labeled by distance d of proton from jellium edge. (a) $r_s = 2$; (b) $r_s = 3$.

and energy ϵ inside the sphere. The physical ideas already expressed in the Anderson framework can readily be incorporated. The inclusion of only a 1s valence orbital on the H atom goes over in the KKR method to retaining only the l=0solution inside the sphere. The idea of a constant self-consistent adatom valence energy ϵ_{eff} leads to the assumption that the l=0 binding strength of the potential inside the sphere be independent of distance from the surface. The radius of the sphere chosen is rather small (actually 1 a.u.), in order to minimize the region of space in which the Schrödinger equation is constrained to an l=0solution. This necessitates taking a somewhat deeper potential inside the sphere than is realistic, but since it is mainly the binding strength of the spherical potential which is important, this is not believed to be serious.

In the case of alkali atoms one tends to base one's thinking on the situation for d at or exceeding the equilibrium distance from the surface. In this region a single alkali atom is largely ionized. and the adatom-surface interaction is not usually considered strong enough to form a resonance with significant bonding character, though it might be strong enough to significantly hybridize the adatom s and p valence orbitals.²² In this situation, shifts in resonance position originate in shifts in ϵ_{eff} from such causes as the image potential or other screening effects rather than from $\Lambda(\epsilon)$ ²³ the "weak-coupling" case of Fig. 1(a) being probably near the truth in the physical region. Considerable interest nevertheless attaches to the resonance width Δ itself. We shall assume that the resonance involves the 2s (in the case of Li) atomic orbital, provided it is reasonably narrow compared with the energy separation of the 2s and 2p orbitals. Accordingly, we again use the KKR model as for hydrogen, modifying the sphere radius and internal potential appropriately; in this case our guide to these is, respectively, the Li atomic radius and the position of the resonance in the first principles calculations,² in an attempt to reproduce correctly the shape of the resonance.

II. FORMALISM

Let H_0 denote the Hamiltonian of the free surface, and v the potential in the neighborhood of the adsorbing atom. We shall assume that v is a spherically symmetric potential which is nonzero only within a sphere of radius R. If we now denote the eigenvalues of the total Hamiltonian Hincluding v by ϵ_n , and those of H_0 by ϵ_k , then the difference in density of states (including spin) introduced by the perturbation v is given by

$$\Delta N(\epsilon) = 2\sum_{n} \delta(\epsilon - \epsilon_{n}) - 2\sum_{k} \delta(\epsilon - \epsilon_{k}) .$$
 (4)

If we now introduce a function $f(\epsilon)$ which is analytic everywhere except at a finite number of poles ϵ_k (the energy eigenvalues of H_0), and whose zeros are at ϵ_n , we can show by use of a well-known theorem of analysis²⁴ that Eq. (2) can be rewritten in the form

$$\Delta N(\epsilon) = 2\pi^{-1} \operatorname{Im} \frac{d}{d\epsilon} \ln f(\epsilon) \,. \tag{5}$$

We shall not give the full expression for $f(\epsilon)$ within the KKR method, but confine ourselves to the case of importance in this paper where only l=0 solutions to the Schrödinger equation inside

the sphere are considered. Let the l=0 solution to the Schrödinger equation inside the sphere at energy ϵ be $\psi_0(r)$, and $G^0(r, r')$ be the Green function $G^0 = (\epsilon - H_0)^{-1}$ belonging to the unperturbed Hamiltonian H_0 ; then a choice for $f(\epsilon)$ is

$$f(\boldsymbol{\epsilon}) = \overline{G}(r,r') \frac{\partial \psi_0(r')}{\partial r'} - \frac{\partial \overline{G}(r,r')}{\partial r'} \psi_0(r'), \qquad (6a)$$

$$\overline{G}(r,r') = \lim_{\xi \to 0^+} \int_{r=R-\xi} dS \int_{r=R-\xi} dS' G^{0}(\overline{\mathbf{r}},\overline{\mathbf{r}}') \,. \quad (6b)$$

Here the integrations are over the surface of the spheres of radius r and r'(r'>r). It is seen that $f(\epsilon)$ is indeed zero at the perturbed eigenvalues ϵ_n [see Eq. (3.10) of Ref. 21], and it has poles at the unperturbed eigenvalues ϵ_k due to the presence of the functions $G^0(\mathbf{\bar{r}}, \mathbf{\bar{r}'})$.

Thus $\Delta N(\epsilon)$ is given in our approximation by

$$\Delta N(\epsilon) = 2\pi^{-1} \operatorname{Im} \frac{d}{d\epsilon} \ln \left(\overline{G}(r, r') \frac{\partial \psi_0(r')}{\partial r'} - \frac{\partial}{\partial r'} \overline{G}(r, r') \psi_0(r') \right).$$
(7)

The great advantage of this method is that it is capable of considering separately the solutions inside the sphere through ψ_0 , and those outside through G^0 , and then to match them at the surface of the sphere. We note here that the KKR method¹² is variational with respect to the ϵ_n and thus to $\Delta N(\epsilon)$; in fact, it minimizes the mismatch at the surface of the sphere. The determination of $\psi_0(r)$ presents no problem; one simply has to solve the Schrödinger equation for the chosen potential v(r). The main difficulty is thus the calculation of the Green function $G^0(\vec{r}, \vec{r}')$. For a free-electron gas with a surface, G^0 is given by the general expression

$$G^{0}(\mathbf{\tilde{r}},\mathbf{\tilde{r}}') = \sum_{\mathbf{\tilde{k}}} \frac{e^{i\mathbf{\tilde{k}} \cdot (\mathbf{\tilde{x}}-\mathbf{\tilde{x}}')}\psi_{k_{z}}(z)\psi_{k_{z}}^{*}(z')}{\epsilon - \epsilon_{\mathbf{\tilde{k}}} + is}, \qquad (8)$$

where capital letters are designed to represent variables parallel to the surface, and lower-case letters to represent variables perpendicular to the surface, $\epsilon_{\vec{k}} = \frac{1}{2}(K^2 + k_z^2)$ in atomic units, and s is an infinitesimal positive quantity. The ψ_{k_z} 's depend on the model of the surface chosen. We have adopted a finite-barrier potential model to describe the surface. The barrier of height V_0 is taken at $z = z_0$. By considerations of charge neutrality of the system, it has been shown that the jellium edge is situated at a distance z_i from the barrier,²⁵ where

$$z_{i} = -\frac{3}{2k_{F}} \left[\frac{\pi}{4} + \left(\frac{k_{0}^{2}}{2k_{F}^{2}} - 1 \right) \sin^{-1} \left(\frac{k_{F}}{k_{0}} \right) - \frac{1}{2} \left(\frac{k_{0}^{2}}{k_{F}^{2}} - 1 \right)^{1/2} \right].$$
(9)

Here $k_0 = (2V_0)^{1/2}$ and k_F is the Fermi wave vector.

There are two possibilities for the wave functions,²⁶ according to whether k_s is greater or less than k_0 . For $k_s < k_0$, the eigenvalue spectrum is nondegenerate and the wave functions are given by

$$\psi_{k_{z}}(z) = \frac{\cos[k_{z}(z-z_{0})-\delta]; \ z < z_{0}}{\frac{k_{z}}{k_{0}}} e^{-q_{z}(z-z_{0})}; \ z > z_{0}.$$
(10)

 δ is a phase shift given by $\tan \delta = -q_x/k_x$ and $q_z = (k_0^2 - k_z^2)^{1/2}$. For $k_z > k_0$ the eigenvalue spectrum is doubly degenerate, and the two linearly independent wave functions are taken to be

$$\psi_{k_{z}}^{(1)}(z) = \begin{cases} \frac{1}{2} \left[e^{ik_{z}(z-z_{0})} + \left(\frac{k_{z}-q'_{z}}{k_{z}+q'_{z}}\right) e^{-ik_{z}(z-z_{0})} \right]; \ z < z_{0} \\ \frac{k_{z}}{k_{z}+q'_{z}} e^{iq'_{z}(z-z_{0})}; \ z > z_{0}, \end{cases}$$
(11)

$$\psi_{k_{z}}^{(z)}(z) = \begin{cases} \frac{(k_{z}q'_{z})^{1/2}}{k_{z} + q'_{z}} e^{-ik_{z}(z-z_{0})}; & z < z_{0} \\ \frac{1}{2} \left(\frac{k_{z}}{q'_{z}}\right)^{1/2} \left[e^{-iq'_{z}(z-z_{0})} + \left(\frac{q'_{z} - k_{z}}{q'_{z} + k_{z}}\right) e^{iq'_{z}(z-z_{0})} \right]; & z > z_{0}, \end{cases}$$

$$(12)$$

and $q'_z = (k_z^2 - k_0^2)^{1/2}$.

These were chosen in such a way that $\psi_{k_z}^{(1)}$ represents the analytic continuation of Eqs. (10) for $k_z > k_0$ in which case $\psi_{k_z}^{(2)}$ is the only possible choice which is linearly independent of $\psi_{k_z}^{(1)}$.

These define the continuum completely. One can now construct the Green's functions by inserting the ψ 's as given by Eqs. (10-12) into Eq. (8). In order to calculate \overline{G} , it is then necessary to expand the ψ 's in terms of spherical harmonics about the sphere center (here taken as the origin), and then keep only the l=0 term in the expansions. One now has to sum over \overline{k} . The integration over \overline{k} is straightforward although rather lengthy and is detailed in the Appendix. There are two possible expressions for $\overline{G}(r, r')$ according to whether the barrier at z_0 lies to the right or to the left of the sphere center at the origin. These expressions are given by

(13)

$$\overline{G}(r,r') = -4\pi j_0(kr) \left(\frac{e^{-ikr'}}{r'} + k_0 j_0(kr') \int_{k/k_0}^{\infty} [2x^2 - 1 - 2x(x^2 - 1)^{1/2}] i e^{-i\alpha x} dx \right) \cdot z_0 > 0$$

and

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$$\overline{G}(r,r') = -4\pi j_0(i\kappa r) \left(\frac{e^{-\kappa r'}}{r'} + k_0 j_0(i\kappa r') \int_{\kappa/k_0}^{\infty} [2x^2 - 1 - 2x(x^2 - 1)^{1/2}] e^{\alpha x} dx \right); \qquad z_0 < 0,$$
(14)

where $k = (2\epsilon)^{1/2}$, $\kappa = [2(V_0 - \epsilon)]^{1/2}$, $\alpha = 2k_0 z_0$, and j_0 is the spherical Bessel function of order zero.

The KKR formalism only permits evaluation of \overline{G} rigorously when the sphere does not overlap the barrier, i.e., $z_0 > R$ or $z_0 < -R$. In practice, continuity of the wave functions for $z \ge z_0$ in Eqs. (10)–(12) should keep the results reasonable for a small amount of overlap. We shall in the following assume the results remain reasonable provided $|z_0| \ge 0.5R$.

Before going on to calculate ΔN , let us look briefly at the properties of $\overline{G}(r,r')$, and first of all let us look at the simple limit $V_0 \rightarrow \infty$. In this case it is easily shown by repeated integration by parts that Eqs. (13) and (14) reduce in the limit $k_0 \rightarrow \infty$ to

$$\overline{G}(r,r') = \begin{cases} -4\pi j_0(kr) \left(\frac{e^{-ikr'}}{r'} - j_0(kr') \frac{e^{-2ikz_0}}{2kz_0} \right); z_0 > 0\\ 0; z_0 < 0 \end{cases}$$
(15)

i.e., the results found in our previous work for an infinite-barrier potential model.¹⁴

In the limit $z_0 \rightarrow \infty$, as in the limit $V_0 \rightarrow 0$, one obtains the result for the Green's function in the case of an impurity in the bulk, if only the s phase shift is taken into account.²⁷ i.e.,

$$\overline{G}(r,r') = -4\pi j_0(kr)e^{-ikr'}/r'.$$
(16)

In the limit $z_0 \rightarrow -\infty$, Eq. (16) is suitably transformed to take account of the change in "local bottom of band" which is in this case at the vacuum level, i.e.,

$$\overline{G}(r,r') = -4\pi j_0(i\kappa r)e^{-\kappa r'}/r' .$$
(17)

Let us now look at the behavior of \overline{G} at low energies for finite $z_0 > 0$. The bulk term in (13) which gives the behavior at small ϵ of the imaginary part of the Green's function for an *s* phase shift in the bulk [see Eq. (16)] is eliminated completely by a term which arises from the presence of the surface (i.e., which depends on z_0), thus giving for the imaginary part of the Green's function an $\epsilon^{3/2}$ behavior at low energies. Or in other words, the atom sees a surfacelike density of states ($\epsilon^{3/2}$) instead of a bulk-like density of states ($\epsilon^{1/2}$).

The high-energy behavior of $\overline{G}(r, r')$ is not quite so simple. $\overline{G}(r, r')$ is an oscillating function of ϵ . The amplitude of the successive oscillations decreases rather slowly as $\epsilon^{-1/2}$. For negative values of z_0 , one sees immediately that the imaginary part of $\overline{G}(r, r')$ is vanishingly small at low energies due to the exponential term in (14) which is very small for $\epsilon/V_0 \ll 1$. At high energies the behavior is rather similar to that found for $z_0 > 0$.

The function $\psi_0(r)$ which appears in (7) is the regular l=0 solution of the Schrödinger equation in r < R at energy ϵ . This function being always real, it is easily shown that Eq. (7) reduces to

$$\Delta N(\epsilon) = 2\pi^{-1} \frac{d\eta}{d\epsilon} \tag{18}$$

and

$$\tan\eta(\epsilon) = \frac{\mathrm{Im}\overline{G}(r,r')\gamma_0 - \mathrm{Im}(\partial/\partial r')\overline{G}(r,r')}{\mathrm{Re}\overline{G}(r,r')\gamma_0 - \mathrm{Re}(\partial/\partial r')\overline{G}(r,r')}, \quad (19)$$

where γ_0 is the logarithmic derivative of ψ_0 calculated at r=R, and the real and imaginary parts of $\overline{G}(r,r')$ and their derivatives with respect to r' are also taken at r=r'=R.

The positions of the resonances are given by the zeros of the denominator of Eq. (19), which occur when

$$\gamma_0(\epsilon) = L_d(\epsilon) , \qquad (20)$$

$$L_d(\boldsymbol{\epsilon}) = \frac{\partial}{\partial r'} \ln \overline{G}(r, r') \big|_{r=r'=R}.$$

Limiting results are

$$L_{\infty} = -\frac{1}{R} - K; \quad \epsilon < V_0 \tag{21}$$

$$L_{-\infty} = \int -\frac{1}{R} - (2|\epsilon|)^{1/2}; \ \epsilon < 0$$
 (22a)

$$\int -\frac{1}{R} - k \tan kR; \quad \epsilon > 0.$$
 (22b)

We notice that Eq. (19) strongly resembles the equation for the phase shift in a bulk impurity scattering problem, to which it reduces if Eq. (16) is substituted for \overline{G} into (19). As in bulk scattering theory, a sharp resonance can occur if the denominator of (19) goes through zero [i.e., (20) is satisfied] when the numerator is small. This does not happen for l=0 bulk resonances as the numerator has the $\epsilon^{1/2}$ behavior which does not vanish rapidly enough at small ϵ , in contrast to the $\epsilon^{3/2}$ behavior for an l=1 resonance.²⁸

In the present problem when $z_0 > R$ (sphere lies_

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inside barrier), as just pointed out above for ImG, the numerator of (19) behaves as $\epsilon^{3/2}$ for small ϵ , i.e., like an l=1 phase shift, so that a well-defined resonance can indeed exist even when the sphere is *inside* the surface. When z < R (sphere outside barrier) the numerator of (19) is attenuated exponentially to an extent increasing with distance from surface and modulus of energy below vacuum. Now a resonance of sharpness increasing with distance from surface can occur. The present formalism thus shows very simply how a resonance can be developed which is at once sharp yet essentially l=0-like inside the sphere.

One notices here also the analogy between our expression for ΔN as given by Eqs. (18) and (19), and its equivalent in the Anderson formulation, i.e., Eq. (1). However, a rigorous mapping of one expression on to the other proves difficult to carry out unambiguously except in the limit where the proton is far outside the surface. In this case we find that the expressions for Δ and Λ in Eq. (1) are

$$\Lambda(\epsilon) \simeq z_0^{-1} A^{-1} \left(\frac{1}{2} - \frac{\epsilon}{V_0} \right) e^{-2\kappa (z_0 - R)} , \qquad (23a)$$

$$\Delta(\epsilon) \simeq -z_0^{-1} A^{-1} \left[\frac{\epsilon}{V_0} \left(1 - \frac{\epsilon}{V_0} \right) \right]^{1/2} e^{-2\kappa(z_0 - R)} , \quad (23b)$$

where

$$A = \left(\frac{d\gamma_0}{d\epsilon} - \kappa^{-1}\right)_{\epsilon = \epsilon_{\text{eff}}}.$$
 (23c)

Here ϵ_{eff} is the energy of the bound state of the well at $z_0 \rightarrow \infty$ (sphere far outside surface), given by the solution of Eq. (20) with $L_d(\epsilon)$ given by Eq. (21).

III. RESULTS

A. Hydrogen

The calculation of η and ΔN depends on the form of the perturbation v(r), which manifests itself through the logarithmic derivative $\gamma_0(\epsilon)$. In fact, $\gamma_0(\epsilon)$ was found to be very little dependent upon the actual shape of the model potentials chosen—we have tried square-well, Yukawa, and exponential potentials—provided that these were taken to be equally strongly binding. We give the results for the form

$$v(r) = -v_0 e^{-r}$$
. (24)

We take R=1 a.u.; In fact, small changes in R have little effect on the results. R should not, however, be taken too large to satisfactorily use a one phase shift model. The only remaining pa-

rameter is thus v_0 , which was chosen so as to give a weakly bound state for the proton in bulk jellium as has been found when $r_s > 1.9$ in first principles calculations.²⁰ A value of $v_0 = 2.7$ a.u. gives the bound state at 0.02 a.u. below the bottom of the band; this is independent of r_s since v is measured with respect to bottom of band. Equation (24) implicitly assumes that v(r) is unchanged (relative to bottom of band) when $z_0 < R$, i.e., sphere outside barrier, an assumption requiring justification. Now most of the barrier potential V_0 is seen from jellium calculations to be made up of exchange-correlation potential, especially at large r_s . Even at $r_s = 2$ the electrostatic contribution is only $\Delta \phi \sim 0.25$ a.u., compared with $V_0 = 0.6$ a.u. It could be argued that for $z_0 > R$ we should increase v(r) by $\Delta \phi$ (a rather small correction for $r_s \gtrsim 3$). However, we argue that since the relatively small sphere radius chosen excludes a considerable portion of the attrative region around the proton which is sampled by the "1s orbital," we should have some compensatory factor which we arbitrarily select by neglecting $\Delta \phi$.

The finite square barrier model has been used as an approximation to the jellium one by Mahan.²⁹ The fact that Mahan required the extreme value $V_0 = \epsilon_{\rm F}$ to fit jellium of $r_s \leq 3$ suggests that the analogy between the finite barrier and jellium models might be better at lower electron densities $r_s \geq 3$. In this context we recall that in the present work we do not employ Mahan's variational pro cedure to determine V_0 but we simply take the value of V_0 as the calculated jellium work function plus Fermi level.

The results of our calculation of $\Delta N(\epsilon)$ based on the potential (24) with $V_0 = 2.7$ a.u. are shown in Figs. 3 and 4 and in Table I. 30 It is necessary to recall that the problem of sphere overlap with the barrier prevents the inclusion of results from our calculation at d values for which $|z_0| > 0.5$ a.u. in Fig. 3 and Table I; in Fig. 4 we have interpolated so as to smoothly fill in the excluded region. There is a striking general agreement between our results and those of the first-principles calculations. Our results give a fairly clearly defined resonance peak in ΔN at most d. The d variation of the maximum in this resonance is seen from Fig. 4 to be in very fair general agreement with that of the first principles calculations for r_s = 2, 3, and 4. Furthermore, the width is narrow at large d, then increases as d decreases, and finally narrows again as the bound state is about to separate just as in the first principle calculations. Quantitatively, Fig. 3 and Table I show that the resonance width is found to be in fair overall accord with the latter except that our calculation cannot reproduce the awkward situation



FIG. 3. $\Delta N(\epsilon)$ in Fig. 2, according to present work. Curves labeled by values of d and by $\Delta_n(\epsilon_{\rm F})$ in parenthesis. (a) $r_s=2$; (b) $r_s=3$.

∆N(€) a.u.⁻¹

in which the sphere is at the barrier. We take this as indicating that the physical model which is the central point of this paper is physically correct.

Notwithstanding the general agreement just mentioned, let us indicate its limitations. First, in the probably rather unstable region of negative dwhere the bound state is about to separate, our resonances are too narrow [see especially the r_s = 2 case in Fig. 3(a)]. Second, there does seem to be a discernible tendency in Table I for our resonance width to reach its maximum at a larger value of d than that found in the first principles cal-



FIG. 4. Energy relative to vacuum level of maximum in resonance peak of ΔN as a function of d for three r_s values. Broken curves—Ref. 5; full curves—present work. Levels at $d=\infty$ shown at right (broken line—Ref. 5, full lines—present work). Fermi levels shown at top left.

culations; this may possibly arise from differences between the jellium and finite barrier models. Third, the choice (24) leads to different potentials v(r) relative to vacuum when r_s varies, so the resonance position converges to different "atomic levels" at $d \rightarrow \infty$ in our model. Here, however, the resonance positions in the first principles calculations (see Fig. 4) still show just such nonconvergent behavior at the largest positive dvalues available, and furthermore seem curiously to be converging to a level well above that given for the neutral H atom in LDF approximation. In this connection there is seen in our $r_s = 2$ resonance position in Fig. 3 to be an analogous small one-body shift upwards at $d \simeq 3$ a.u. relative to $d = \infty$.³⁰ The upward shift is clearly seen analytically to occur from Eqs. (3) and (23a) when the level ϵ_{eff} lies above $\frac{1}{2}V_0$. However, this effect

			<i>r</i> _s = 2				
$d^{\mathbf{a}}$	-1.0	-0.3	0.0	0.7	1.1	2.0	3.0
$E_{r_1}^{b}$	-15.2	•••	-11.6	•••	-7.3	-5.6	•••
$E_{r_2}^{c}$	-15.7	-14.0	•••	-12.0	-8.2	-6.0	$_{-5.4}$
$2\Delta_1^{d}$	1.8	•••	5.0	•••	4.4	2.5	•••
$2\Delta_2^{e}$	0.7	3.3	•••	4.0	4.2	2.5	1.2
$\Delta \eta(\epsilon_F)^{f}$	0.9	1.0	•••	1.4	1.4	1.6	1.9
<i>r</i> _s = 3							
d	-1.0	-0.5	0.0	0.5	1.0	1.5	3.0
Er_1	-8.6	-8.3	-7.8	_7.1	-6.1	-5.4	•••
Er_2	-8.8	-8.2	_7.7	•••	-6.2	$_{-4.1}$	-2.5
$2\Delta_1$	0.4	0.9	1.5	2.6	2.0	1.7	•••
$2\Delta_2$	0.4	0.8	1.6	•••	2.1	3.0	1.0
$\Delta \eta(\epsilon_{F})$	1.1	1.1	1.1	•••	1.3	1.0	0.2
<i>r</i> _s =4							
d	-1.0	-0.5	0	0.5	1.0	1.5	3.0
Er_1	-5.9	-5.6	-5.2	-4.9	-4.5	•••	•••
Er_2	-6.0	-5.9	-5.6	-5.0	• • •	-4.4	-1.9
$2\Delta_1$	0.3	0.5	0.5	0.7	0.7	•••	•••
$2\Delta_2$	0.1	0.3	0.5	0.9	•••	1.6	1.2
$\Delta \eta(\epsilon_F)$	1.2	1.2	1.3	1.2	•••	1.2	0.2

TABLE I. Resonance widths and positions.

 $^{\mathbf{a}}d$ in a.u.

^b Energy of maximum in resonance from Ref. 5 (eV).

^c Energy of maximum in resonance—present work (eV). d Full width at half-maximum of resonance from Ref. 5 (eV).

^eFull width at half-maximum of resonance—present work (eV).

^fAccording to present work.

seems too small to explain the whole of the effect in the first-principles results just alluded to. Finally, there arises the important question of the area under the $\Delta N(\epsilon)$ curves, which will now be discussed.

In Fig. 5 we illustrate $\Delta n(\epsilon)$, as defined in Sec. I, for $r_s = 2$ ($r_s = 3$ is very similar except for a slightly lower relative position of ϵ_F). Curves such as that for d=1.1 may be regarded as illustrating the phenomenon of an "incomplete resonance".^{28,31} However, we gain further information by using the Anderson-model discussion in Sec. I. It is seen that, apart from the lack of a common intersection, curves d = 3.0, 1.1, and -1.0 in Fig. 5 have a strong resemblence to curves c = 0.08, 0.65, and 1.2, respectively, of Fig. 1(b). We therefore believe it is reasonable to interpret them in the same way. We could therefore conclude that at d = 3.0 we have an atomiclike resonance, at d=1.1 a partly bonding and partly atomiclike one, whereas at d = -1.0 we have a virtual bonding state. It is remarkable that Fig. 5 resembles so closely curves derived from a



FIG. 5. $\Delta n(\epsilon)$ vs ϵ at $r_s=2$. Curves labeled by values of d.

narrow-band Anderson model (Fig. 1).

By comparison of Fig. 5 with Fig. 1(b), it also seems that ϵ_{eff} and also ϵ_F are reasonably near the band center. In accordance with the discussion in Sec. I, the quantity $\Delta n(\epsilon_F)$ should then afford a single number giving information on the bonding character. If $\Delta n(\epsilon_F)$ is near unity there is an occupied localized bonding state or occupied resonance of strongly bonding character, with unoccupied anti-bonding states, implying a degree of covalency. On the other hand, if $\Delta n(\epsilon_F)$ is near 2 or 0, it implies, respectively, a full or empty atomic resonance. Figures for $\Delta n(\epsilon_F)$ are added to Fig. 3 in brackets and are found in Table I.

It is seen that at $r_s = 2$ there is moderate bonding character $[\Delta n(\epsilon_F) = 1.36]$ at d = 1.1, the Jellium equilibrium distance. The d value is reduced on the Al close-packed surfaces,^{3,5} so although $\Delta n(\epsilon_F)$ is more or less unchanged at a smaller value of d such as 0.7, we expect from Fig. 5 that the resonance has more bonding character. Covalent character increases further as indicated by $\Delta n(\epsilon_F)$ approaching unity at negative d. At large d, $\Delta n(\epsilon_F)$ approaches 2, corresponding to an occupied atomic resonance. Similar behavior is found at $r_s = 3$ except t at the atomic resonance is unoccupied. The important conclusion of this discussion is that for a practical system such as H on Al there is something resembling a covalent bond in that the occupied resonance has strongly bonding character.

Of course, the numerically calculated Δn values in Fig. 2 are required to be strictly unity by selfconsistency. Ours differ from unity due to projection on the l=0 subspace. It is assumed here that the effects neglected by us are mainly of the nature of *screening* and thus information about the *bond* is best derived from the approximate Δn . However, one may wonder whether the whole of such a notable disagreement in area $\Delta n(\epsilon_F)$ be-tween, say the case $r_s = 2$, d = 2 in Figs. 2(a) and 3(a) can be explained in this way.

B. Lithium

In the case of lithium there is the additional complication of a $1s^2$ core. We consider only the Li valence shell and thus include the core by means of a "model potential." For simplicity, we have chosen a square-well perturbing potential rather than (24), since the core should eliminate the attractive central region from the model potential. Thus our v(r) is

$$v(r) = -v_0; \quad r \le R. \tag{25}$$

R should ideally be the atomic radius of Li, but as for H a somewhat smaller *R* and larger v_0 was used to reduce the region of space constrained to an l=0 solution. *R* was varied in order to determine the role it plays in the calculation. The remaining parameter v_0 was then chosen such that the position of the resonance coincides with that found by Lang and Williams in their first-principles calculations² for Li adsorption on jellium ($r_s = 2$).

The results at the Lang and Williams equilibrium distance of 2.5 a.u. from the jellium $edge^{1,2}$ are illustrated in Fig. 6, and compared to those of the first-principles calculations.² The curves are labeled by the *R* values. A change in *R* is thus not seen to produce a drastic variation in the resonance width. The best agreement with the calculation of Lang and Williams was obtained for *R* = 2.5 a.u. In comparison, we note that the atomic radius of Li is 2.9 a.u. The corresponding value of v_0 was given by $v_0 = 0.45$ a.u. This particular



FIG. 6. $\Delta N(\epsilon)$ for Li adsorbed on jellium at $r_s=2$. Broken curve—Ref. 2; full curve—present work. The latter are labeled by the value of R used.

well gives an l=0 bound state situated at about 3 eV below the vacuum level, in comparison to the ionization energy of 5.4 eV for Li. There is thus an upward shift of 2.4 eV of that level attributable to the image force or other screening effect. The value of the resonance width at this value of R= 2.5 a.u. is about 2.5 eV. This makes it larger than the 2s-2p energy separation of 1.85 eV for Li,³² which necessarily means that these two levels are strongly hybridized—an effect which has been predicted for Cs adsorption on transition metals.²² Our l=0 calculation is thus inadequate and must be extended to take account of the l=1 solution inside the sphere.

If the distance from the jellium edge d is allowed to vary (R and v_0 being kept fixed at R = 2.5 and $v_0 = 0.45$ a.u.), one finds that whereas the position of the resonance hardly varies at all, the width changes dramatically from about 4.5 eV at d=2 a.u. to about 1.5 eV at d=3 a.u. One should remark at this stage that the former situation is poorly described within our model, not only because of the necessity of inclusion of an l=1 solution inside the sphere, but also because there is a certain amount of overlap between the sphere and the surface barrier. (i.e., $z_0 = 0.7$ a.u.). On the other hand, our model should adequately describe the case d=3 a.u.

Inclusion of the substrate ionic pseudopotentials in first-order perturbation theory was shown to lead to a reduction of d to d=2.1 a.u.,² for adsorption of Li in a three fold site on Al(111). This value of d is still much larger than the ionic radius of Li (1.2 a.u.).

It is also of interest to consider the case of lower-electron-density substrates such as the case $r_s = 3$, since this should represent reasonably well the sp band of Ag or of Ni ($r_s = 3.08$ corresponding to 0.6s electrons per Ni atom). The parameters representing the adatom properties are taken from above (R = 2.5 a.u., $v_0 = 0.45$ a.u.). A new feature of the results for $r_s = 3$ is the presence of a downward shift of the resonance position as d is decreased, which was absent in the case $r_s = 2$. This downward shift may be regarded as a bonding shift and indicates the possibility that adsorption might be less ionic for these lowerdensity substrates.

IV. CONCLUSION

We have derived a virtually analytic expression for the change in density of states $\Delta N(\epsilon)$ when a monovalent atom is in interaction with a surface approximated by the finite square barrier potential. The atom is restricted to have only an *s*-like valence orbital; this is achieved by keeping only the l=0 solution in the muffin-tin-KKR technique. The model is applied to hydrogen chemisorption on jellium, for which elaborate self-consistent first principles calculations are available. The potential inside the hydrogen muffin tin, chosen by consideration of the situation for hydrogen deep inside jellium, is kept independent both of distance d from jellium edge and of r_s . Good overall agreement with the first-principles calculations was then found, involving reproduction of the dramatic variation of width and position of the resonances as a function of d, for $r_s = 2$, 3, and 4. The assumed potential seems, however, to break down if the hydrogen is too far outside the surface. We are therefore able to confirm a simple chemical picture of the resonances occurring in the first-principles calculations as essentially 1s in character. We are also able to allot bonding character to the resonances. They are found to be substantially

atomic in character when the proton lies well outside the surface, but to develop strong bonding character near the equilibrium distance.

In applying the model to lithium chemisorption on jellium, again good results were obtained for the essentially atomic-like 2s resonance by comparison with first-principles calculations. Extension of our method to treat problems not so far dealt with in first-principles calculations, such as adsorption of the higher alkalis, is under way.

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APPENDIX: CALCULATION OF G(r,r')

1. $z_0 > 0$

The integration over \mathbf{k} must be split into two contributions arising from the $k_z < k_0$ and $k_z > k_0$ regions. After expansion of the plane waves in spherical harmonics, and truncation of this expansion beyond the first term, we find

$$\overline{G}(r,r') = 8\pi^{2} \sum_{k} \frac{j_{0}(kr)j_{0}(kr')}{\epsilon - \epsilon_{k} + is} \left[1 + \left(\frac{2k_{g}^{2}}{k_{0}^{2}} - 1\right) \cos 2k_{g} z_{0} + \frac{2k_{g}}{k_{0}} \left(1 - \frac{k_{g}^{2}}{k_{0}^{2}} \right)^{1/2} \sin 2k_{g} z_{0} \Theta(k_{0} - k_{g}) - \frac{2k_{g}}{k_{0}} \left(\frac{k_{g}^{2}}{k_{0}^{2}} - 1\right)^{1/2} \cos 2k_{g} z_{0} \Theta(k_{g} - k_{0}) \right],$$
(A1)

where Θ is the unit step function.

The calculation of the imaginary part of $\overline{G}(r, r')$ presents no difficulty, and it is found that $\text{Im}\overline{G}(r, r')$ can be written in terms of a single integral which in turn can be evaluated numerically,

$$\operatorname{Im}\overline{G}(r,r') = 4\pi k j_{0}(kr) j_{0}(kr') \left(1 + \frac{k_{0}}{k} \int_{0}^{k/k_{0}} \left\{ \left[2x^{2} - 1 - 2x(x^{2} - 1)^{1/2} \Theta(x - 1) \right] \cos \alpha x + 2x(1 - x^{2})^{1/2} \sin \alpha x \Theta(1 - x) \right\} dx \right\}.$$
(A2)

We now look at the real part of $\overline{G}(r, r')$. After changing the order of integration, we find

$$\operatorname{Re}\overline{G}(r,r') = 2 \int_{0}^{\infty} \frac{j_{0}(yr)j_{0}(yr')}{\epsilon - y^{2}/2} y^{2} dy + k_{0} \int_{0}^{\infty} \left\{ \left[2x^{2} - 1 - 2x(x^{2} - 1)^{1/2} \Theta(x - 1) \right] \cos \alpha x + 2x(1 - x^{2})^{1/2} \sin \alpha x \Theta(1 - x) \right\} dx \int_{x}^{\infty} \frac{j_{0}(yr)j_{0}(yr')}{\epsilon - y^{2}/2} y \, dy \,.$$
(A3)

The first term can be integrated analytically. The integration with respect to y in the second term can be written in terms of sine and cosine integrals. These are regular functions everywhere in the complex plane except for the singularities of logarithmic nature of the cosine integrals.³³ One can then, by use of the residue theorem, rewrite these in terms of simpler integrals to find

$$\operatorname{Re}\overline{G}(r,r') = 4\pi j_0(kr) \left(kn_0(kr') - k_0 j_0(kr') \int_{k/k_0}^{\infty} \left\{ \left[2x^2 - 1 - 2x(x^2 - 1)^{1/2} \Theta(x - 1) \right] \sin \alpha x - 2x(1 - x^2)^{1/2} \Theta(1 - x) \cos \alpha x \right\} dx \right),$$
(A4)

where n_0 is the spherical Neumann function of order zero. If we now make use of the identity

$$\int_0^\infty \left\{ \left[2x^2 - 1 - 2x(x^2 - 1)^{1/2} \Theta(x - 1) \right] \cos \alpha x + 2x(1 - x^2)^{1/2} \sin \alpha x \Theta(1 - x) \right\} dx = 0,$$
 (A5)

we can rewrite Eqs. (A2) and (A4) into equation (13) of the text.

2. $z_0 < 0$

Once more there are two contributions to $\overline{G}(r, r')$ arising from the $k_z < k_0$ and $k_z > k_0$ regions. The wave function for $k_z < k_0$ is a real exponential; it can, however, be rewritten in terms of plane waves which we then treat in the manner described above. In this way we find

$$\overline{G}(r,r') = 8\pi^2 \sum_{\vec{k}} \frac{j_0(iqr)j_0(iqr')}{\epsilon - \epsilon_{\vec{k}} + is} \left[\frac{k_z^2}{k_0^2} e^{2q_z z_0} \Theta(k_0 - k_z) + \frac{1}{2} \left(\frac{k_z}{q_z'} \right) \left(1 + \frac{q_z' - k_z}{q_z' + k_z} \cos 2q_z' z_0 \right) \Theta(k_z - k_0) \right], \tag{A6}$$

where $q = [k_0^2 - (k_z^2 + \kappa^2)]^{1/2}$.

The imaginary part of $\overline{G}(r, r')$ is then given by

$$\operatorname{Im}\overline{G}(r,r') = \begin{cases} 4\pi j_0(i\kappa r) j_0(i\kappa r') k_0 \int_{\kappa/k_0}^{\prime} 2x(1-x^2)^{1/2} e^{\alpha x} dx ; & E < V_0 \\ 4\pi j_0(i\kappa r) j_0(i\kappa r') k_0 \left(\frac{i\kappa}{k_0} + \int_{i\kappa/k_0}^{\infty} [2x^2 + 1 - 2x(1+x^2)^{1/2}] \cos\alpha x \, dx \right) ; & E > V_0 . \end{cases}$$
(A7)

In order to calculate the real part of $\overline{G}(r, r')$, we have to change the order of integration as in the case of $z_0 > 0$. There is a supplementary difficulty in this case due to the fact that we must integrate along all of the real axis and part of the imaginary axis as well. After some manipulation we find

$$\operatorname{Re}\overline{G}(r,r') = \begin{cases} -4\pi j_0(i\kappa r) \left(\frac{e^{-\kappa r'}}{r'} + k_0 j_0(i\kappa r') \int_{\kappa/k_0}^{\infty} [2x^2 - 1 - 2x(x^2 - 1)^{1/2} \Theta(x - 1)] e^{\alpha x} dx \right); & E < V_0 \\ -4\pi j_0(i\kappa r) \left(\kappa n_0(i\kappa r') + k_0 j_0(i\kappa r') \int_{i\kappa/k_0}^{\infty} [2x^2 + 1 - 2x(x^2 + 1)^{1/2}] \sin\alpha x \, dx \right); & E > V_0. \end{cases}$$
(A8)

Equation (14) now follows immediately from Eqs. (A7) and (A8).

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