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Applications of the Hellmann-Feynman theorem in surface physics

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We present a generalized version of the Hellmann-Feynman theorem which is then applied to problems in surface physics. In particular, we derive a number of exact results for an atom adsorbed on a surface. The limitations of the theorem are also discussed.

I. INTRODUCTION

For many years, there has been considerable interest in the Hellmann-Feynman (HF) theorem.[1–3] Various specific formulations of the HF theorem have been given that are thought to give maximum insight into its physical content or to be most suited for practical calculations for a variety of different systems. A well-known special case is the electrostatic theorem,[2] which shows that the force of the electrons in a molecule on a nucleus in it can be expressed solely in terms of the electron density of the molecule. Another intriguing result, due to Foldy,[4] expresses the binding energy of an atom (as a function of its atomic number) solely in terms of the electrostatic potential of the electrons at the position of the nucleus. Recently, Budd and Vannimenus[5] derived an important relation between the electrostatic potential at the surface of jellium metal and the bulk electron energy based on the HF theorem. We will return to the above examples in the context of the present work, but, of course, there have been many other valuable applications of the HF theorem.[6]

The Hellmann-Feynman theorem has always been fascinating because of its basic simplicity; the idea that it could lead to rather simple formulas applying to many-body systems is very attractive. On the other hand, it has always been a subject of much debate as to just how much physics such formulas contain and even more so as to their usefulness in quantitative analyses. In this paper this question arises, and we will discuss it in the end. Meanwhile we shall derive a generalized version of the electrostatic theorem, that, however simple, to our knowledge, has not been given before. It unifies many well-known results, for example those mentioned above. But, beyond that and more importantly, we feel this formulation is eminently suited as a starting point for the derivation of many more applications, a fact on which we would like to focus attention by giving some new results for an atom adsorbed on a surface.

The paper is organized as follows. In Sec. II the generalized version of the electrostatic theorem is derived and discussed. In Sec. III the relation between this general result and the specific examples mentioned above is clarified, while in Sec. IV we demonstrate its power to obtain many new results by applying it to the problem of adsorption of an atom on a jellium surface. Finally, in Sec. V, we will discuss the question concerning the practical usefulness of our new results and that of others which might be obtained in a similar fashion.

II. GENERALIZED ELECTROSTATIC THEOREM

In its general form both the Hellmann-Feynman (HF) theorem and its proof are extremely simple. Let the Hamiltonian $\mathcal{H}$ of a system depend on an arbitrary parameter λ, and let $\psi(\lambda)$ be any eigenstate of $\mathcal{H}(\lambda)$ with eigenvalue $E(\lambda)$. It then follows immediately from the normalization condition $\langle\psi(\lambda)|\psi(\lambda)\rangle = 1$ for all λ, that

$$\frac{\partial E(\lambda)}{\partial\lambda} = \langle\psi(\lambda)\left|\frac{\partial\mathcal{H}}{\partial\lambda}\right|\psi(\lambda)\rangle \ . \tag{2.1}$$

This is the general Hellmann-Feynman theorem.

Over the years this theorem has been applied to many specific systems, one of which is that of a molecule, where the electronic eigenstates are to be determined given a fixed (Born-Oppenheimer approximation) nuclear charge distribution

$$\rho(\vec{R}) = |e| \sum_{\alpha} Z_\alpha \delta(\vec{R} - \vec{R}_\alpha) \ . \tag{2.2}$$

(Z_α is the atomic number of nucleus α, and $\vec{R}_\alpha$ is its position.) If one considers the parameter λ in Eq. (2.1) to be a coordinate of one nucleus, say β, then upon a small change of this coordinate one finds from Eq. (2.1)

$$-\frac{\partial E}{\partial \vec{R}_\beta} = Z_\beta e^2 \int n(\vec{r}) \frac{\vec{r} - \vec{R}_\beta}{|\vec{r} - \vec{R}_\beta|^3} d\vec{r} + e^2 \sum_{\alpha\neq\beta} Z_\alpha Z_\beta \frac{\vec{R}_{\alpha\beta}}{R_{\alpha\beta}^3} \ , \tag{2.3}$$

with

$$n(\vec r) \equiv N \int |\psi(\tau', \vec r; \{\vec R_\alpha\})|^2 \, d\tau'$$

being the electron density in the electronic eigenstate $\psi(\tau; \{\vec R_\alpha\})$ at fixed configuration $\{R_\alpha\}$ of the nuclei. The notation means: τ represents the coordinates and spin variables of all N electrons in the molecule, and τ' is all variables represented by τ except the position variables $\vec r$ of one electron. Expression (2.3) is known as the *electrostatic theorem.* It says, that the force $-\partial E/\partial \vec R_\beta$ on a nucleus β can be given in terms of the exact electron density alone, hence being determined by electrostatics only, with the understanding, of course, that the correct electron density $n(\vec r)$ has to be found from the solution of the Schrödinger equation

$$\left[-\frac{h^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{r_{ij}} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec R_\alpha - \vec r_i|} + \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}} \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} \right] \psi(\tau, \{R_\alpha\}) = E \psi(\tau, \{R_\alpha\}) \; . \qquad (2.4a)$$

The electrostatic theorem is an illustrative example of two aspects of all special cases (and their specific formulation) derived from the general HF theorem. On the one hand it gives a qualitative physical picture of the implications of the HF theorem. On the other hand, one has to know the exact solution of a quantum-mechanical problem—in this case the exact molecular electron density—since the HF theorem holds only for exact eigenstates. Since the real difficulty is to find this density, not the computation of the force on a nucleus once the density is known, whether the HF theorem is ever of practical use is debatable, i.e., whether it can sometimes actually help one solve the Schrödinger equation itself, or give quantitative physical information without full knowledge of its solution.

We shall now generalize the electrostatic theorem, to describe the case of a small arbitrary variation $\delta\rho$ in an arbitrary positive charge distribution $\rho(\vec R)$. Also, it will appear to be modified in such a way that it does not involve the electron density, as in expression (2.3), but rather the electrostatic potential. Let $\mathcal{H}_\rho$ be the Hamiltonian of a system of N electrons and an arbitrary fixed positive charge distribution $\rho(\vec R)$

$$\mathcal{H}_\rho = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{1}{r_{ij}} - \sum_i \int d\vec R \, \frac{\rho(\vec R)}{|\vec R - \vec r_i|} + \frac{1}{2} \int d\vec R \, d\vec R' \, \frac{\rho(\vec R)\rho(\vec R')}{|\vec R - \vec R'|} \; . \qquad (2.4b)$$

In the following we use atomic units, $m_e = h = |e| = 1$ [cf. Eq. (2.4a)]. Every eigenvalue $E[\rho]$ of the Schrödinger equation,

$$\mathcal{H}_\rho \psi(\tau;\rho) = E[\rho] \psi(\tau;\rho) \; ,$$

is a functional of ρ. Upon a small arbitrary change $\delta\rho$ one finds in complete analogy with the standard derivation of the Hellmann-Feynman theorem,[2]

$$\frac{\delta E[\rho]}{\delta\rho(\vec r)} = -\phi_\rho(\vec r) \; , \qquad (2.5a)$$

with

$$\phi_\rho(\vec r) = \int \frac{n_\rho(\vec r') - \rho(\vec r')}{|\vec r - \vec r'|} \, d\vec r' \qquad (2.5b)$$

the exact electrostatic potential, and

$$n_\rho(\vec r) = N \int \psi^*(\tau', \vec r; \rho) \psi(\tau', \vec r; \rho) \, d\tau' \qquad (2.5c)$$

the electron number density in the stationary state $\psi(\tau;\rho)$. Or, in integral form, the change ΔE in the total energy of the system, initially in *any* eigenstate, upon a small change $\delta\rho$ in the positive charge distribution, is given by

$$\Delta E = -\int \delta\rho(\vec r) \phi_\rho(\vec r) \, d\vec r \; , \qquad (2.6)$$

which follows from a straightforward application of perturbation theory.

It is interesting to compare this result with classical electrodynamics.[7] In that case, the change ΔE in the total energy upon any small change δN of the *total* charge distribution $N(\vec r)$ is given by

$$\Delta E = -\int \delta N(\vec r) \Phi(\vec r) \, d\vec r \; . \qquad (2.7)$$

Here $\Phi(\vec r)$ is the electrostatic potential [same conventions as in Eq. (2.5b)] corresponding to the initial charge distribution $N(\vec r)$ and given by Poisson's equation

$$\nabla^2 \Phi(\vec r) = 4\pi N(\vec r) \; .$$

It should be recognized that expression (2.6) is also a classical result. The quantum mechanics of the problem (consisting of the calculation of the correct electron density from the wave function) has been completed and the classical limit is taken: the expectation value $n_\rho(\vec{r})$ of Eq. (2.5c) in the state $\psi(\tau;\rho)$ is actually identified with the macroscopic electron density by virtue of the fact that there is a large number of electrons in the system, and the electrostatic potential $\phi(\vec{r})$ defined by Eq. (2.5b) satisfies Poisson's equation. That expressions (2.6) and (2.7) are different at all is caused by the fact that in the former case the change is made starting from an eigenstate of the whole system, in the latter by starting from an arbitrary state. So, all the Hellmann-Feynman theorem says is that if one changes the total charge distribution $\delta N = \delta\rho + \delta n_\rho$ starting from an electronic eigenstate at fixed positive charge density ρ, the energy changes to order $\delta\rho$ but only to order $(\delta n)^2$ in the electronic part, as can be seen from perturbation theory. Therefore expression (2.6) is just a special case of Eq. (2.7) as indicated above.

Although expression (2.6) is just a simple modification of Eq. (2.3), the usefulness of this specific formulation to surface problems has gone largely unnoted. Some applications which are special cases of Eq. (2.6) have, however been given[4,5] and we shall discuss those in Sec. III. Also, the general form [Eq. (2.6)] has been obtained for the ground state.[8] In that work the proof of Eq. (2.6) relies on the Hohenberg-Kohn theorem[9] for the ground-state energy. Invoking this powerful theorem for the ground state facilitates the proof and makes it considerably more elegant; however, its validity is not required to prove Eq. (2.6), since the latter follows from perturbation theory from all eigenstates, as in the Hellmann-Feynman theorem. The main point we would like to make, however, concerning the general expression (2.6) is that it lends itself to many immediate applications because $\delta\rho(\vec{r})$, the change in the positive charge density, occurs in the integrand. This is a parameter that one can control externally in contrast to the case of the ordinary formulation of the electrostatic theorem which involves the electron density, a quantity to be calculated first from the (often forbiddingly difficult) quantum-mechanical problems before one can perform the integral. Therefore, as we shall demonstrate in Sec. IV, the electrostatic theorem given by Eq. (2.6) gives numerous simple applications of the HF theorem even before one ventures on the solution of the many-electron problem. In the end, all of these will, of course, involve the exact electrostatic potential. So, the issue, whether the HF theorem can be of any practical use in solving or circumventing the Schrödinger problem, remains as always. However, the mere simplicity of the formulas in terms of the electrostatic potential in contrast to, e.g., expression (2.3) justifies the hope that they may be more useful for practical purposes than many given in the past. We shall return to this question in Sec. V.

III. DERIVATION OF WELL-KNOWN RESULTS FROM THE GENERAL FORMULA

The simplest application of the general formula (2.6) is Foldy's result[4] relating to the binding energy of an atom as a function of its atomic number Z. Consider an atom with nuclear charge Z located at $\vec{R}$. Then, upon changing the charge of the nucleus by ΔZ, i.e., $\delta\rho(\vec{r}) = \Delta Z\,\delta(\vec{r}-\vec{R})$, one immediately obtains from Eq. (2.6) $\Delta E = -\Delta Z\,\phi(\vec{R};Z)$, or

$$\frac{\partial E}{\partial Z} = -\phi(\vec{R};Z) \; . \tag{3.1}$$

Here, $\phi(\vec{R};Z)$ is the potential energy of the electrons in the unperturbed atom at the position of the nucleus. Some remarks should be made, that often apply to results derived from Eq. (2.6). While our derivation of Eq. (2.6) demands that the number of *electrons* be fixed, there is no requirement for $\int \delta\rho(\vec{r})\,d\vec{r}$ to be zero. Hence, the system need not remain neutral upon performing a small change in the positive density ρ. Integrating the left-hand side of Eq. (3.1) between Z and $Z+1$, we obtain the difference in energy between a singly ionized atom of atomic number $Z+1$ and a neutral atom of atomic number Z. Now, $\phi(\vec{R};Z)$ is the electrostatic potential of a neutral atom supposedly known as a function of Z. Upon *integrating* the right-hand side from Z to $Z+1$, we then make an error, since $\phi(\vec{R};Z)$ as an interpolation between integer values of Z and $Z+1$ corresponds to a neutral system, where the number of electrons is kept equal to the number of protons, as pointed out by Foldy. Another point to be mentioned is that, according to Eq. (2.6), $\phi(\vec{R};Z)$ is the total electrostatic potential, which also contains an infinite part due to the nucleus, since it is evaluated at $\vec{R}$. This is due to the fact that the nucleus is treated as a classical point charge. Whenever such an infinite contribution occurs, it should simply be discarded,[10] so that in the present case $\phi(\vec{R};Z)$ is the potential (energy) of the electrons at the position of the nucleus. A similar result for molecules derived by Wilson[11] can also be obtained immediately from Eq. (2.6).

Another important and straightforward application is the derivation of the usual form of the electrostatic theorem for a molecule [expression (2.3)]. If we change the x coordinate of one of the nuclei in a molecule, say β with charge Z_β at position $\vec{R}_\beta$, we have

$$\delta\rho(\vec{r}) = -Z_\beta\delta(\vec{r}-\vec{R}_\beta) + Z_\beta\delta(x-(X_\beta+\delta X_\beta)) \times\delta(y-Y_\beta)\delta(z-Z_\beta) \; .$$

Substitution in Eq. (2.6) immediately gives

$$\Delta E = Z_\beta\phi(\vec{R}_\beta) - Z_\beta\phi(x_\beta+\delta X_\beta, Y_\beta, Z_\beta) \; ,$$

or

$$\frac{\partial E}{\partial X_\beta} = -Z_\beta \left(\frac{\partial \phi}{\partial X_\beta} \right)_{\vec{R}_\beta} . \tag{3.2}$$

Here ϕ depends parametrically on the positions and charges of all nuclei. For clarity, we do not indicate this dependence. Since

$$\phi(\vec{r}) = -\sum_\alpha \frac{Z_\alpha}{|\vec{r}-\vec{R}_\alpha|} + \int \frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d\vec{r}\,' ,$$

one has

$$\left(\frac{\partial \phi}{\partial x} \right)_{\vec{R}_\beta} = -\sum_{\alpha \neq \beta} \frac{Z_\alpha (X_\alpha - X_\beta)}{|\vec{R}_\alpha - \vec{R}_\beta|^3} + \int \frac{n(\vec{r}\,')(x' - X_\beta)}{|\vec{R}_\beta - r'|^3} d\vec{r}\,'$$

and

$$\frac{\partial E}{\partial X_\beta} = \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta (X_\alpha - X_\beta)}{R^3_{\alpha\beta}} - Z_\beta \times \int \frac{n(\vec{r}\,')(x' - X_\beta)}{|\vec{R}_\beta - \vec{r}\,'|^3} d\vec{r}\,' .$$

This is the usual form of the electrostatic theorem [cf. Eq. (2.3)]. Note that, as in the first example, we have to discard the infinite self-energy part of the potential due to nucleus β at $\vec{R}_\beta$.

A third, very beautiful application is related to the jellium model of a metal. Consider a slab of jellium (of volume V and uniform positive background density ρ_0), then, as is shown by Budd and Vannimenus,[5] one obtains

$$\frac{1}{V} \frac{dE}{d\rho_0} = \phi_0(\rho_0) - \bar{\phi}^V(\rho_0) . \tag{3.3}$$

Here E/V is the bulk energy per unit volume, $\phi_0(\rho_0)$ is the value of the electrostatic potential at the surface of the slab, and $\bar{\phi}^V$ is the average electrostatic potential over the volume. Specifically for the ground state, E is (fairly) well known from the theory of the uniform electron gas, hence the value of the electrostatic potential at the surface (relative to its average value over V) can be obtained from Eq. (3.3). This is actually an example where the Hellmann-Feynman theorem leads to an exact result (the value of ϕ_0) quite directly, that can be obtained only with much work numerically from the solution of the Schrödinger equation.[12] Budd and Vannimenus have also given the expression (2.6) in a subsequent paper,[8] but as we mentioned earlier its validity for *all* stationary states does not follow from their proof. [They did prove their result (3.3) for all stationary states, but this involved application of the HF theorem (2.1) with respect to the thickness of the jellium slab]. More importantly, we like to make the point that many more applications of Eq. (2.6) in the spirit of Eq. (3.3) can be given, as long as $\delta\rho(\vec{r})$ is simple enough and suitably chosen. We will now turn to such applications.

IV. APPLICATION TO THE ADSORPTION OF AN ATOM ON A JELLIUM METAL SURFACE

Let us now derive some new results with respect to adsorption of an atom on a jellium metal surface, that follow very easily from Eq. (2.6). We consider the geometry of Fig. 1(a). A jellium slab of uniform positive charge density ρ_0 with volume V extends from $x = -L$ to $x = 0$ along the x axis, the surfaces being planes perpendicular to it. An atom of nuclear charge $Z|e|$ is adsorbed on the surface $x = 0$, its nucleus being located at $x = d$. The energy E of this system is a function of the four parameters ρ_0, Z, d, and L. Because of the simplicity of the geometry, results for the dependence of E on these parameters are easily obtained from Eq. (2.6). The electrostatic potential [convention of Eq. (2.5b)] is cylindrically

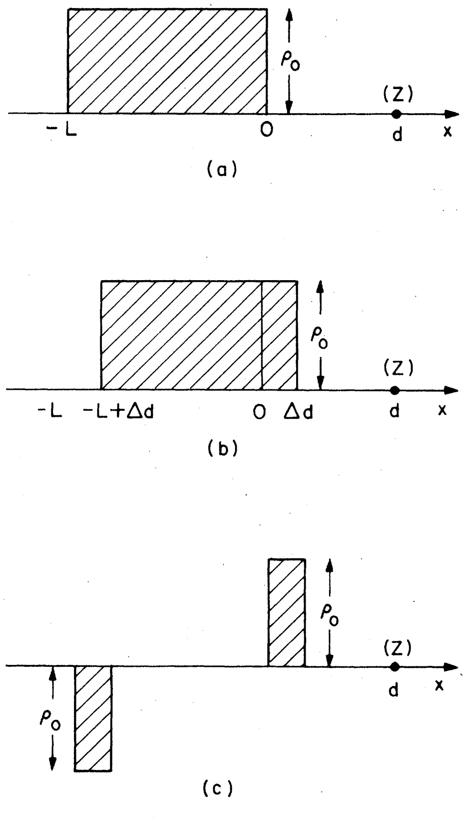

FIG. 1. (a) Jellium slab of uniform positive charge density ρ_0, volume V, extending from $-L$ to 0 on the x axis with an atom of nuclear charge $Z|e|$ at $x = d$. (b) New configuration found by moving the entire jellium slab Δd along the x axis. (c) $\delta\rho(\vec{R})$.

symmetric and, with charges $\delta\rho(\vec{r})$ of the same symmetry, we have

$$\Delta E = -\int \phi(\vec{R};\rho_0,Z,d,L)\delta\rho(\vec{R})\, d\vec{R} = -2\pi \int_{-\infty}^{\infty} dx \int_0^{\infty} dr\, r\phi(x,r;\rho_0,Z,d,L)\delta\rho(x,r)\, dr \quad (r^2=y^2+z^2) .$$

1. Distance of the atom to the surface

A relation for the energy as a function of the distance d of the adsorbed atom to the surface can be obtained by considering the following small change $\delta\rho(\vec{R})$ [see Figs. 1(b) and (c)]:

$$\begin{aligned} &\delta\rho(x,r) = -\rho_0 , \quad -L \leqslant x \leqslant -L+\Delta d , \\ &\delta\rho(x,r) = +\rho_0 , \quad 0 \leqslant x \leqslant \Delta d , \\ &\delta\rho = 0 , \quad \text{elsewhere} . \end{aligned}$$

One simply displaces the slab by a small amount Δd. Then, without denoting the dependence on parameters that are irrelevant in this case

$$\begin{aligned} \Delta E = E(d-\Delta d) - E(d) &= -2\pi \int_{-L}^{-L+\Delta d} dx \int dr\, r(-\rho_0)\phi(x,r;d) - 2\pi \int_0^{\Delta d} dx \int dr\, r(\rho_0)\phi(x,r;d)\, dr \\ &\simeq 2\pi\rho_0\Delta d \int dr\, r\phi(-L,r;d) - 2\pi\rho_0\Delta d \int dr\, r\phi(0,r;d) . \end{aligned}$$

Hence

$$-\frac{1}{\rho_0}\left(\frac{\partial E}{\partial d}\right)_{\rho_0,Z,L} = 2\pi \int [\phi(-L,r;d) - \phi(0,r;d)]\, r\, dr ,$$

or

$$\frac{1}{S\rho_0}\left(\frac{\partial E}{\partial d}\right)_{\rho_0,Z,L} = \bar{\phi}^S(d) - \bar{\phi}_0^S . \tag{4.1}$$

Here $\bar{\phi}^S(d)$ is the average of the exact electrostatic potential over the surface *with* the atom at $x=d$, $\bar{\phi}_0^S$ is the average of the exact electrostatic potential over the surface without the atom present [since for $L\to\infty$, $\phi(-L,r,d)$ is the potential of an unperturbed metal surface]. S is the surface area. E is the total energy of the system, but the same relation holds for the interaction energy $E_{\text{int}} = E - E_M - E_A$, where E_M and E_A are the total energy of the metal and atom, respectively, when infinitely far apart, since neither E_M nor E_A depends on d. Since

$$\lim_{d\to\infty} \bar{\phi}^S(d) = \bar{\phi}_0^S$$

the derivative of E with respect to d tends to zero as $d\to\infty$, as it should.

One may also displace the atomic nucleus by Δd in the x direction so that

$$\delta\rho(\vec{R}) = -Z\delta(\vec{R}-\vec{d}) - Z\delta(\vec{R}-(\vec{d}+\Delta\vec{d})) .$$

Then

$$\begin{aligned} \Delta E &= Z\int d\vec{R}\, \phi(\vec{R};\vec{d})[\delta(\vec{R}-\vec{d}) - \delta(\vec{R}-(\vec{d}+\Delta\vec{d}))] \\ &= Z[\phi(x=d,r=0;d) - \phi(x=d+\Delta d, r=0;d)] , \end{aligned}$$

or

$$\left(\frac{\partial E}{\partial d}\right)_{\rho_0,Z,L} = -Z\left(\frac{\partial\phi(x,r=0;d)}{\partial x}\right)_{x=d} . \tag{4.2}$$

2. Thickness of the slab

The change in energy as a function of the thickness L of the slab (keeping ρ_0, d, and Z constant) is simply obtained from [see Fig. 2(a)]

$$\delta\rho(x,r) = \begin{cases} \rho_0 , & -L-\Delta L \leqslant x \leqslant -L , \\ 0 , & \text{otherwise} . \end{cases}$$

Then

$$\begin{aligned} \Delta E &= E(L+\Delta L) - E(L) \\ &= -2\pi\rho_0 \int_{-L-\Delta L}^{-L} dx \int dr\, r\phi(x,r;L) \\ &\simeq -2\pi\rho_0\Delta L \int dr\, r\phi(-L,r;L) , \end{aligned}$$

or, in the limit of a very thick slab ($L\to\infty$)

$$\left(\frac{\partial E}{\partial L}\right)_{Z,\rho_0,d} = -\rho_0 S\bar{\phi}_0^S(\rho_0) , \tag{4.3}$$

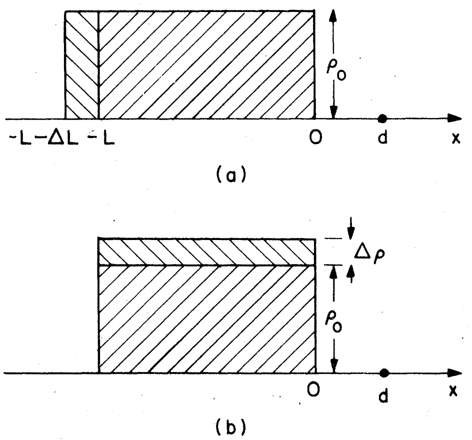

FIG. 2. (a) Jellium slab is increased in width by ΔL. (b) Positive charge density is increased by $\Delta\rho$.

where $\bar{\phi}_0^S$ as defined in Eq. (4.1). Unlike the case of Eqs. (4.1) and (4.2), where the system remains charge neutral upon the change $\delta\rho$, here $E(L+\Delta L)$ is the energy of a charged system, since the total positive charge has been increased or decreased (depending on whether ΔL is positive or negative), while the total number of electrons remains constant throughout the change. Therefore, we run into the same situation as discussed by Foldy[4] with respect to the atomic binding energy.

3. *Uniform background density*

For this case consider

$$\delta\rho(x,r)=\begin{cases}\Delta\rho\ , & -L\leqslant x\leqslant 0\ ,\\ 0\ , & \text{otherwise}\ ,\end{cases}$$

as in Fig. 2(b). Then

$$\Delta E = E(\rho_0+\Delta\rho)-E(\rho_0) = -2\pi\int_{-L}^{0}dx\int dr\, r\phi(x,r;\rho_0)\ ,$$

or

$$\left(\frac{\partial E}{\partial\rho_0}\right)_{Z,d,L} = -V\bar{\phi}^V(\rho_0,Z,d,L)\ . \tag{4.4}$$

Here $\bar{\phi}^V$ is the average of the exact electrostatic potential over the volume of the metal sample. As in Eq. (4.3) the change $\delta\rho$ does not connect two charge neutral systems, since $E(\rho_0+\Delta\rho)$ corresponds to a positively or negatively charged metal depending on $\Delta\rho$ being positive or negative. Because of this fact neither Eq. (4.3) nor Eq. (4.4) seem particularly interesting by themselves. One would rather like an expression for the change in energy of an atom adsorbed on a surface upon a change of the uniform background density keeping the metal neutral. Such an expression is easily obtained from Eqs. (4.3) and (4.4) (see Fig. 3).

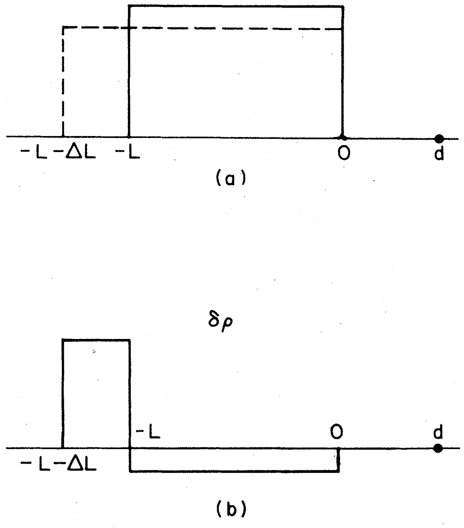

FIG. 3. (a) Full curve is the positive charge density before; the dashed curve is the density after the change $\Delta\rho$. This change conserves total charge. (b) $\Delta\rho$.

$$\delta E = \left(\frac{\partial E}{\partial\rho_0}\right)_{Z,d,L}\Delta\rho + \left(\frac{\partial E}{\partial L}\right)_{Z,d,\rho_0}\Delta L = -V\bar{\phi}^V\Delta\rho - \rho_0 S\bar{\phi}_0^S\Delta L\ .$$

Now, we have to choose $\Delta L = -L\Delta\rho/\rho_0$ in order to keep the metal neutral. Hence

$$\frac{1}{V}\left(\frac{\delta E}{\delta\rho_0}\right)_{d,Z} = \bar{\phi}_0^S(\rho_0) - \bar{\phi}^V(\rho_0,Z,d)\ . \tag{4.5}$$

In the limit

$$\lim_{d\to\infty}\bar{\phi}^V(d,\rho_0,Z) = \bar{\phi}_0^V(\rho_0)\ ,$$

the volume average of a metal without the atom, this result coincides with the Budd and Vannimenus formula (3.3). For the interaction energy $E_{\rm int}=E-E_M(\rho_0)-E_A$ we obtain, using Eq. (3.3) for $E_M(\rho_0)$,

$$\frac{1}{V}\left(\frac{\delta E_{\rm int}}{\delta\rho_0}\right)_{d,Z} = \bar{\phi}_0^V(\rho_0) - \bar{\phi}^V(d,\rho_0,Z)\ , \tag{4.6}$$

i.e., the change in the interaction energy of a given atom upon a change in the background density equals the difference in the average electrostatic potential over the sample with and without the atom adsorbed. The thickness of the sample, chosen to be very large, becomes an irrelevant parameter in the result (4.6).

4. *Charge of the atomic nucleus*

If one changes the nuclear charge by ΔZ,

$$\delta\rho(x,r) = \Delta Z\,\delta(\vec{R}-\vec{d})$$

and

$$\Delta E = -\Delta Z\,\phi(x=d, r=0; d, Z)$$

or

$$\left(\frac{\partial E}{\partial Z}\right)_{\rho_0,d,L} = -\phi(x=d, r=0; d, Z, \rho_0, L)\ . \tag{4.7}$$

Again, the system does not remain neutral under $\delta\rho$. It may be more interesting to consider a change that does keep the system neutral, or in the case of Eqs.

(4.5) and (4.6).

$$\frac{\delta E}{\delta Z}\Delta Z \equiv \left(\frac{\partial E}{\partial Z}\right)_{\rho_0 dL}\Delta Z + \left(\frac{\partial E}{\partial L}\right)_{\rho_0 dZ}\Delta L, \text{ with } \Delta L = -\Delta Z/\rho_0 S$$
$$= [\bar{\phi}_0^S(\rho_0) - \phi(x=d,r=0;d)]\Delta Z ,$$

or

$$\left(\frac{\delta E}{\delta Z}\right)_{\rho_0,d} = \bar{\phi}_0^S(\rho_0) - \phi(x=d,r=0;\rho_0\, dZ) . \quad (4.8)$$

One can also consider the change in *interaction* energy upon changing the atomic number by ΔZ keeping the whole system neutral

$$\delta E_{\text{int}} = \delta E - [E_M(N-\Delta Z;L-\Delta L;\rho_0) - E_M(N;L;\rho_0)] - [E_A(Z+\Delta Z, Z+\Delta Z) - E_A(Z,Z)] .$$

Here $E_M(N;L,\rho_0)$ is the total energy of an unperturbed neutral metal slab with N electrons (length L, positive background density ρ_0). $E_A(Z_1,Z_2)$ is the total energy of a free atom with Z_1 electrons and atomic number Z_2.

Using Eq. (4.8) for δE, Eq. (4.3) for the metallic part, and Eq. (3.1) for the atomic part, one has

$$\left(\frac{\delta E_{\text{int}}}{\delta Z}\right)_{\rho_0,d} = [\phi_A(x=d,r=0;Z) - \phi(x=d,r=0;\rho_0,d,Z)] + \delta\Phi - \delta I . \quad (4.9)$$

Here ϕ_A is the electrostatic potential of a free atom, $\delta\Phi$ is the change in energy of an unperturbed neutral metal upon adding ΔZ electrons to it, and δI is the change in energy of a free neutral atom upon removing ΔZ electrons from it. Apart from the latter quantities, which depend on the metal or atom only, the change in interaction energy is given by the difference of the electrostatic potential at the position of the atomic nucleus with and without the metal surface present. It is amusing to note the similarity of the results (4.9) and (4.6); however, a direct integration of the right-hand side of Eq. (4.9) (if it were known as a function of Z), to obtain E_{int} as a function of Z, is at best a crude approximation, just as in the case with Foldy's result for the free-atom upon integration of Eq. (3.1).

V. DISCUSSION

We have demonstrated in Secs. II–IV how the generalized electrostatic theorem (2.6) is at the root of various well-known specific formulations, and also how eminently suited it may be for the derivation of new results on various physical systems. As an example of some importance we considered the case of an atom adsorbed on a very simple surface, but one might think of many others in the field of surface physics, e.g., adsorption of monolayers, adsorption on surfaces with simple steps and kinks,[13] etc. However, the question regarding the practical importance of all such results still remains to be discussed. We confine our remarks to the adsorption problem.

First of all, it would be instructive to have some models of adsorption for which the electrostatic potential and various other properties can be calculated exactly. We could then see which information can also be obtained from our results of Sec. IV and whether or not it is gained more easily. For the present case we were able to find only one such example, that of a plasmalike medium I (with background dielectric constant ϵ_0) separated by a planar boundary S from a dielectric medium II (with dielectric constant ϵ) in which a point charge q is embedded at a distance d from S (see Fig. 4).[14,15] The plasma is described by Poisson's equation $\Delta\phi = p^2\phi$, where p is the Thomas-Fermi screening wave vector. For this system some important features can be obtained readily from our result (4.2). The electrostatic

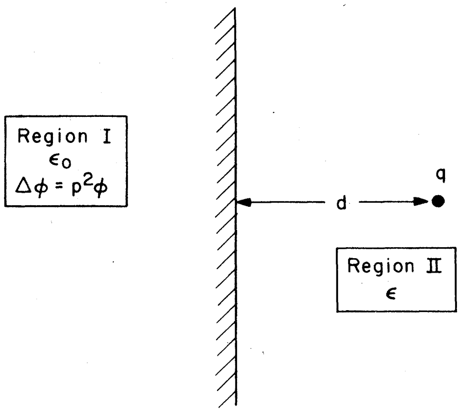

FIG. 4. A charge q embedded in a dielectric with dielectric constant ϵ near a plasma half space which is described by a Thomas-Fermi wave vector p.

potential in medium II is given by[14,15] [convention of Eq. (2.5b)]

$$\phi_{\text{II}}(s,r;d) = -\frac{q}{\epsilon}\int_0^\infty dk\, J_0(kr)e^{-k|x-d|} - \frac{q}{\epsilon}\int_0^\infty dk\, J_0(kr)e^{-kx}U(k,d)\ ,$$

with

$$U(k,d) = \frac{(\epsilon/\epsilon_0)k - (k^2+p^2)^{1/2}}{(\epsilon/\epsilon_0)k + (k^2+p^2)^{1/2}}e^{-kd}$$

In the limit of $r \to 0$ and $x \to d$, the point where we have to evaluate ϕ in order to apply Eq. (4.2), the first term becomes the singular self-energy part of the point charge q, and has to be discarded. Hence, applying Eq. (4.2) for this system, we have

$$\left[\frac{\partial E}{\partial d}\right]_{p,q} = -q\left[\frac{\partial\phi(x,r=0;p,q,d)}{\partial x}\right]_{x=d}$$

$$= \lim_{\substack{r\to 0\\ x\to d}} \frac{q^2}{\epsilon}\int_0^\infty dk\, J_0(kr)(-k)\,U(k,d)e^{-kx}$$

$$= \frac{q^2}{\epsilon}\int_0^\infty dk\, k\frac{(k^2+p^2)^{1/2} - (\epsilon/\epsilon_0)k}{(k^2+p^2)^{1/2} + (\epsilon/\epsilon_0)k}e^{-2kd}\ .$$

From this result the qualitative conclusion follows immediately: if $\epsilon < \epsilon_0$, the integrand is positive definite and hence no adsorption minimum can occur; for $\epsilon > \epsilon_0$ the integrand changes sign and an adsorption minimum may occur. If we scale the distance by $k = px$, then

$$\frac{\partial E}{\partial(2pd)} = \frac{q^2p}{2\epsilon}\int_0^\infty dx\, x\left[\frac{(x^2+1)^{1/2} - (\epsilon/\epsilon_0)x}{(x^2+1)^{1/2} + (\epsilon/\epsilon_0)x}\right]e^{-(2pd)x}\ .$$

In the limit of an ideal metal: $\epsilon_0 \to \infty$ or $\epsilon/\epsilon_0 \to 0$, we have

$$\frac{\partial E}{\partial(2pd)} = \frac{q^2p}{2\epsilon}\int_0^\infty dx\, xe^{-(2pd)x}$$

$$= \frac{q^2p}{2\epsilon}\frac{1}{(2pd)^2}\ ,$$

or upon integration

$$E(d) - E(\infty) = \frac{q^2p}{2\epsilon}\int_\infty^{2pd}\frac{dx}{x^2} = -\frac{q^2}{\epsilon(4d)}\ ,$$

which is the image potential energy of interaction for a point charge at distance d from an ideal flat metal surface. If one calculates the above integral numerically for various values of ϵ/ϵ_0 the results of Fig. 3(a) of Ref. 15 are reproduced. However simple, this example shows that important information can be obtained directly from the results of Sec. IV very easily; notably, in this case, one is able to say under what conditions an adsorption minimum will *not* occur. It seems possible, that in more complicated problems some physical results can be obtained from the formulas of Sec. IV, that are much harder to arrive at otherwise. In fact, the Budd-Vannimenus theorem is a perfect example of this with respect to the jellium metal surface problem.

This brings us to another case to be made for a serious look at simple expressions following from Eq. (2.6). In the case of atomic binding energies there may be, at this point, not much use anymore for a result like the one given by Foldy, since one is able to treat the atomic-electron problem in a very sophisticated manner within the framework of the Hartree-Fock approximation (and beyond). However, for the adsorption problem the state of the art of deriving the interaction potential directly from the electronic structure (i.e., by essentially solving the Schrödinger equation) is still much less satisfactory. In this context, it appears that results like those of Sec. IV may at this stage be very useful in more than one respect. First of all, they may serve as self-consistency criteria for sophisticated numerical solutions of the interaction potential, in the same way as Eq. (3.3) does for numerical calculations of the electronic structure of the jellium metal surface.[5,8] Second, with full theoretical understanding of the adsorption phenomenon currently lacking, parametric solutions of this problem may lead to important qualitative understanding. In this case the electrostatic potential would be a known function of some parameters, for which the relations in Sec. IV then pose self-consistency conditions. Again, drawing a parallel with the jellium surface problem, such approaches have provided very useful steps in the understanding of the jellium surface[16] and work along these lines involving the Budd-Vannimenus theorem (3.3) is still being done.[17]

Finally, as we noted earlier, the fact that the HF theorem holds for *exact* eigenstates (or the exact electrostatic potential) only, restricts its applicability in some respects. It is well known that substantial errors may be introduced, if it is applied to directly calculate energy differences upon changing a parameter in the Hamiltonian while using an *approximate* eigenstate (or approximate potential), since then the energies may change linearly with the electron density as well. On the other hand, even approximate potentials may give surprisingly good results when compared with experiment (for instance in the case of

Foldy's formula for the atomic binding energy based on Hartree or Thomas-Fermi theory for the potential). It is possible that such agreement may turn out to be fortuitous, but this should be assessed for each case separately. We feel that the possibility of direct calculation of adsorption energies from the results of Sec. IV with the aid of *approximate* electrostatic potential should therefore not be neglected.

We have not underscored the discussion remarks above by giving an application to a model complex enough to be realistic which would thus require substantial numerical work. Such an application is outside the scope of the present paper, but is clearly very important to determine the ultimate practical significance of our results.

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[1] H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Leipzig, 1937); R. P. Feynman, Phys. Rev. 56, 340 (1939).

[2] See for example, C. Cohen-Tannoudji, B. Diu, and F. Laloë, *Quantum Mechanics* (Wiley, New York, 1977), p. 1192.

[3] B. M. Deb, Rev. Mod. Phys. 45, 22 (1973).

[4] L. L. Foldy, Phys. Rev. 83, 397 (1951).

[5] H. F. Budd and J. Vannimenus, Phys. Rev. Lett. 31, 1218 (1973).

[6] See, e.g., Ref. 3 for a review.

[7] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1966), p. 123.

[8] J. Vannimenus and H. F. Budd, Solid State Commun. 15, 1739 (1974).

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

[10] L. D. Landau and E. M. Lifshitz, *Classical Theory of Fields* (Pergamon, New York, 1962), p. 101.

[11] E. Bright Wilson, J. Chem. Phys. 36, 2232 (1962).

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

[13] L. L. Kesmodel and L. M. Falicov, Solid State Commun. 16, 1201 (1975).

[14] D. M. Newns, J. Chem. Phys. 50, 4572 (1969); Phys. Rev. B 1, 3304 (1970); P. Lert and J. Weare, J. Chem. Phys. 68, 2221 (1978); 68, 5010 (1978); J. Phys. C 11, 1865 (1978).

[15] A. A. Kornyshev, A. I. Rubinshtein, and M. A. Vorotyntsev, Phys. Status Solidi B 84, 125 (1977).

[16] J. R. Smith, Phys. Rev. 181, 522 (1969).

[17] C. Q. Ma and V. Sahni, Phys. Rev. B 16, 4249 (1977), and references therein.