Self-consistent screening of diatomic molecules in an electron gas

R. Díez Muñoz and A. Salin
Laboratoire de Physico-Chimie Moléculaire, UMR 5803 CNRS, Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence Cedex, France
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We use density-functional theory to calculate the electronic density induced by a diatomic molecule in a free-electron gas, as well as the embedding energy. We perform the calculations for two molecules, H₂ and LiH. We study the dependence of the results on parameters such as the internuclear distance or the mean electronic density of the medium. We discuss the evolution of the system as the medium electronic density is modified with the help of the induced density of levels. We show that the response of the medium is sensitive to the presence of an electric-dipole moment in the isolated molecule. The electron gas screens the interaction between the two centers of the molecule, but can also play a role in transferring charge between them. We show that the shape of the embedding energy variation can be related with different types of molecular adsorption. [S0163-1829(99)02227-4]

I. INTRODUCTION

Understanding the adsorption and desorption mechanisms of particles (atoms and molecules) at gas/solid interfaces is crucial to characterize the chemical properties of surfaces. The dependence of measurable quantities on parameters such as the temperature, the incoming trajectory or, in the case of molecules, the rotational, and vibrational state, makes it difficult to reach a global understanding of the processes taking place. Furthermore, the large number of degrees of freedom and the complex geometry makes any theoretical approach to the problem quite involved.

The theoretical study of the interaction between the particle and the surface is usually divided in two steps: the adiabatic calculation of the electronic properties of the system (and, in particular, of the potential energy) and the dynamics of the particle, using either classical or quantum mechanics. Nonadiabatic corrections can also be included. This paper is dedicated to the first part of the problem, i.e., the electronic properties of a molecule when interacting with a surface. Recent approaches to the problem have succeeded in performing sophisticated \textit{ab initio} calculations, based, for example, on cluster\textsuperscript{1,2} or periodic\textsuperscript{3-5} models. Beside the important computational-effort required, the latter approach makes it difficult to extract general information from the results obtained for a specific system.

Another approach to the problem is the embedding model, in which the electronic properties of the whole surface are only approximately reproduced, but the spatial region localized at the vicinity of the external particle is reasonably well described. Originally developed to study impurities at metal vacancies,\textsuperscript{8,9} the immersion of an atom in a jellium\textsuperscript{10,11} or at a jellium surface\textsuperscript{12-14} has shown to be a good qualitative (and often also quantitative) representation of chemisorbed atoms at metal surfaces. Upon this basic picture, nonlocal effects can be subsequently included in a perturbative way, following the effective-medium ideas.\textsuperscript{15} The embedding concept has also been applied to different physical problems, such as molecular bonding\textsuperscript{16} and induced reconstruction of surfaces.\textsuperscript{17}

To our knowledge, the only molecule for which calculations based on the embedding approach have been published is the H₂ molecule. Some of them are based on the embedding of the molecule in a homogenous jellium\textsuperscript{18,19} and some others on the embedding at a jellium surface.\textsuperscript{20,21} The H₂-surface problem has also been studied by representing the molecule-surface interaction in terms of the embedding of one of the atoms of the molecule into the electronic density created by the sum of the surface electronic density profile and the electronic density associated with the other atom of the molecule.\textsuperscript{22}

In this paper, we present a general method to study the embedding of any dimer in a free-electron gas. By contrast, with most previous calculations that depended on the \textit{a priori} choice of a basis set, our method is parameter free. We illustrate the potentiality of the method by two examples: H₂ and LiH. The latter allows us to show the differences in the electron gas response when the embedded molecule is asymmetric.

The embedding of a molecule in a jellium is a helpful model to understand the interaction processes between a molecule and a metal surface. This model can complement the information extracted from more sophisticated calculations. Its main advantage is that the real situation is substituted by a simpler and well-defined problem that can be rigorously treated. The parameters defining the problem can be controlled without much effort. The effects derived from the approach of the molecule to the surface can be simulated by increasing the electronic density of the homogeneous jellium. The internuclear distance between the nuclei is easily varied. Good asymptotic limits are found: a molecule in vacuum, when decreasing the jellium electronic density, and two embedded atoms, when increasing the molecule internuclear distance. On the other hand, orientation effects are not included.

This paper is organized as follows: the theoretical framework is developed in Sec. II. We present results for two different examples: the H₂ molecule (Sec. III) and the LiH molecule (Sec. IV). We discuss in the latter sections the influence of the electronic structure of the isolated molecule...
(and, more precisely, of its dipole moment) on the jellium response. We show that each molecule can be associated with a different type of adsorption mechanism, depending on the structure of the embedding-energy curves. Finally, we dedicate Sec. V to conclusions.

Atomic units are used throughout unless otherwise stated.

II. THEORETICAL MODEL

As stated, our analysis is based on the embedding of a diatomic molecule in a jellium, i.e., a uniform background of positive charges in which the electrons move. The mean electronic density of the medium is called \( n_0 \) (\( n_0 = 3/4 \pi r_0^3 \)) and the distance between the two nuclei of the molecule is \( d \) (\( d = 2a \)). We focus our attention on the induced electronic density around the nuclei and on the embedding energy. Both are defined below.

We treat the problem within density-functional theory. The mathematical framework is summarized in the present section. Further details of the calculation can be found in Ref. 23, where a similar formalism is applied to a different problem: the energy loss of a low-energy particle inside a free-electron gas.

Following the Kohn-Sham scheme,24 we need to solve a set of one-electron equations

\[
\left\{-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r})\right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \tag{1}
\]

The total electronic density is obtained from the \( \psi_i(\mathbf{r}) \) orbitals by a sum over occupied states

\[
n(\mathbf{r}) = n^{\text{bound}}(\mathbf{r}) + n^{\text{cont}}(\mathbf{r}) = \sum_{i \in \text{occ}} |\psi_i(\mathbf{r})|^2, \tag{2}
\]

where \( n^{\text{bound}}(\mathbf{r}) \) refers to the electronic density associated with the Kohn-Sham states \( \psi_i(\mathbf{r}) \) with \( \epsilon_i < 0 \) and \( n^{\text{cont}}(\mathbf{r}) \) corresponds to the states with \( \epsilon_i = k^2/2 > 0 \). The zero of energy is chosen so that

\[
\lim_{r \to \infty} V_{\text{eff}}(\mathbf{r}) = 0. \tag{3}
\]

The Kohn-Sham orbitals are developed using the spherical-harmonic basis set

\[
\psi_i(\mathbf{r}) = \sum_{l,m} \frac{U_{l,m,i}(\mathbf{r})}{r} Y_l^m(\Omega_r). \tag{4}
\]

The one-electron effective potential \( V_{\text{eff}}(\mathbf{r}) \) is composed of three terms: the external potential \( V_{\text{ext}}(\mathbf{r}) \), the Hartree potential \( V_{\text{Hart}}(\mathbf{r}) \), and the exchange-correlation potential \( V_{\text{xc}}(\mathbf{r}) \). In our problem, the external potential is the Coulomb potential of the two nuclear charges \( Z_1 \) and \( Z_2 \). We expand \( V_{\text{ext}}(\mathbf{r}) \) in terms of Legendre polynomials

\[
V_{\text{ext}}(\mathbf{r}) = \frac{Z_1}{|\mathbf{r} - \mathbf{a}|} - \frac{Z_2}{|\mathbf{r} + \mathbf{a}|} = \sum_{r} [Z_1 + (-1)^r Z_2] (r <) r P_r(\cos \theta), \tag{5}
\]

where \( r_+ = \min(r,a) \) and \( r_- = \max(r,a) \). Only a finite number of terms \( \nu < \nu_{\text{max}} \) is kept in the numerical solution of the problem. We discuss this approximation later on.

The Hartree potential

\[
V_{\text{Hart}}(\mathbf{r}) = \int \frac{d^3 r' \Delta n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \tag{6}
\]

is caused by the induced electronic density \( \Delta n(\mathbf{r}) = n(\mathbf{r}) - n_0 \), since the homogeneous electronic density \( n_0 \) is compensated by the uniform positive background (jellium model).

The exchange-correlation potential \( V_{\text{xc}}[n(\mathbf{r})] \) is calculated using the spin-independent parametrization of Gunnarsson and Lundqvist.25 The potential \( V_{\text{xc}}(\mathbf{r}) \) in Eq. (1) is the change in exchange-correlation potential caused by the presence of the molecule

\[
V_{\text{xc}}(\mathbf{r}) = V_{\text{xc}}[n(\mathbf{r})] - V_{\text{xc}}[n_0]. \tag{7}
\]

As done for the external potential, the total effective potential \( V_{\text{eff}}(\mathbf{r}) \) is expanded in terms of Legendre polynomials. We keep the same number of terms \( \nu_{\text{max}} \) used in the expansion of \( V_{\text{ext}}(\mathbf{r}) \)

\[
V_{\text{eff}}(\mathbf{r}) = \sum_{\nu=0}^{\nu_{\text{max}}} V_{\nu}(r) P_\nu(\cos \theta). \tag{8}
\]

With all these ingredients, the problem is solved iteratively. The iterative process is started when the effective potential \( V_{\text{eff}}(\mathbf{r}) \) and the induced electronic density \( \Delta n(\mathbf{r}) \) are self-consistently determined. The main practical difficulty comes from the resolution of the Kohn-Sham equations for a nonspherical potential. The cylindrical symmetry ensures that \( m \) (but not \( l \)) is a good quantum number. The expansion of the effective potential \( V_{\text{eff}}(\mathbf{r}) \) in terms of Legendre polynomials [Eq. (8)] allows us to transform Eq. (1) into a system of coupled equations. For each fixed value of \( \epsilon_i \) and \( m \) we have

\[
\left[ \frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} + \epsilon_i \right] u_{l,m,i}(r) = \sum_{l'} U_{l'l'i}^{m}(r) u_{l',m',i}(r), \tag{9}
\]

where the coupling term \( U_{l'l'i}^{m}(r) \) between the different \( l \)-partial waves is

\[
U_{l'l'i}^{m}(r) = \int d\Omega_r V_{\text{eff}}(\mathbf{r}) Y_{l'm'}(\Omega_r)[Y_{lm}(\Omega_r)]^* \tag{10}
\]

The system is solved after truncation of the partial-wave expansion [Eq. (4)] at a maximum value \( l_{\text{max}} \). We determine \( l_{\text{max}} + 1 \) linearly independent solutions of the problem, i.e., \( l_{\text{max}} + 1 \) sets \( \{u_{l,j,m,i}(r), l = 0, \ldots, l_{\text{max}}\} \), with \( j \) varying from 0 to \( l_{\text{max}} \). The required solution of the system can always be expressed as a linear combination of these linearly independent solutions

\[
u_{l,m,i}(r) = \sum_{j=0}^{l_{\text{max}}} \gamma_{j} u_{l,j,m,i}(r) \tag{11}
\]
for each value of \( l \) from 0 to \( l_{\text{max}} \). We remark that the coefficients \( \gamma_j \) do not depend on \( l \). They obviously depend on \( m \) and \( \epsilon_i \), but the dependence is not explicitly written. We determine \( \gamma_j \) by imposing the correct asymptotic conditions to the wave functions.\(^{23}\) The obtention of the \( \gamma_j \) coefficients uniquely determines the radial wave functions \( u_{l,m,i}(r) \) and, subsequently, the \( \psi_i(r) \) orbitals, solution of the Kohn-Sham equations. We calculate from these orbitals the electronic density. The latter is expanded in terms of Legendre polynomials

\[
n(r) = \sum_{\nu=0}^{2l_{\text{max}}} n_\nu(r) P_\nu(\cos \theta).
\] (12)

The \( n_\nu(r) \) coefficients are obtained from

\[
n_\nu(r) = \frac{1}{2\pi} \frac{2(2\nu+1)}{2} \int d\Omega_s P_\nu(\cos \theta) \left[ \sum_{i} |\psi_i(r)|^2 \right] \\
= \frac{1}{4\pi r^2} \sum_{l,m} \sum_{l'} \binom{l}{m} \binom{l'}{-m} u_{l,m,i}(r) u_{l',m,i}(r),
\] (13)

where the angular coefficients are defined in terms of Wigner 3j symbols

\[
\begin{aligned}
\binom{l}{m} \binom{l'}{-m} &= (-1)^m (2\nu+1)(2l+1)^{1/2} \\
\times (2l'+1)^{1/2} &\begin{pmatrix} l' & l & \nu \\ 0 & m & -m \\ 0 & m & 0 \end{pmatrix}.
\end{aligned}
\] (14)

In Eq. (13), the sum over \( i \) and \( m \) runs over occupied states. In the case of continuum states, the sum is converted into an integral over the three-dimensional \( k \) space up to the Fermi level \( k_F \). As the \( \gamma_j \) coefficients defining the radial wave functions \( u_{l,m,i}(r) \) through Eq. (11) do depend on the solid angle \( \Omega_k \), so does the integrand.\(^{25}\) This angular integral can be evaluated analytically.

A useful magnitude that reflects the effects specifically associated with the embedding is the electronic density difference \( \delta n(r) \) defined as the difference between the total electronic density of the joined molecule/jellium system and the sum of the electronic densities of the independent molecule and jellium systems. \( \delta n(r) \) accounts for the displacement of electronic charge due to the coupling between the molecule and the jellium

\[
\delta n(r) = n_{\text{mol+jell}}(r) - n_0 - n_{\text{mol}}(r) = \Delta n(r) - n_{\text{mol}}(r).
\] (15)

One of the aims of this paper is to point out the influence of the molecular dipole moment on the jellium response. We quantify these effects by calculating the electric dipole moment \( \mu \) of the induced electronic density along the axis of the molecule

\[
\mu = \int d^3r \left[ \sum_{\nu=0}^{2l_{\text{max}}} \Delta n_\nu(r) P_\nu(\cos \theta) \right] (r \cos \theta) \\
= \frac{4\pi}{3} \int dr r^3 \Delta n_1(r).
\] (16)

We separate two contributions in the dipole moment \( \mu \): \( \mu_{\text{bound}} \) coming from the one-electron Kohn-Sham bound states (\( \epsilon_i < 0 \)) and \( \mu_{\text{cont}} \) coming from the continuum states (\( \epsilon_i > 0 \)).

The influence of the external electronic environment on the molecular bonding is better characterized with the help of the embedding energy \( E_{\text{emb}} \), defined as the difference between the energy of the molecule/jellium system \( E_{\text{mol+jell}} \) and the sum of the energies of the two isolated systems \( E_{\text{mol}} \) and \( E_{\text{jell}} \)

\[
E_{\text{emb}} = E_{\text{mol+jell}} - E_{\text{jell}} - E_{\text{mol}} \\
= E[n(r)] - E[n_0] - E[n_{\text{mol}}(r)].
\] (17)

The energy functional \( E[n] \) is composed of three terms: the kinetic energy, the electrostatic energy, and the exchange-correlation energy. By substitution, we find that the difference between \( E_{\text{mol+jell}} \) and \( E_{\text{jell}} \) is

\[
E_{\text{mol+jell}} - E_{\text{jell}} \\
= \sum_{i \in \text{bound}} \epsilon_i + \int_{k < k_F} d^3k \frac{k^2}{2} \int d^3r |\psi_i(r)|^2 - |\psi_i^0(r)|^2 \\
- \int d^3r n(r) V_{\text{eff}}(r) \\
- \int d^3r \{n(r)\epsilon_{\text{xc}}[n(r)] - n_0\epsilon_{\text{xc}}[n_0]\} \\
- \int d^3r \Delta n(r) V_{\text{ex}}(r) \\
+ \frac{1}{2} \int d^3r \int d^3r' \frac{\Delta n(r) \Delta n(r')}{|r-r'|},
\] (18)

where \( \psi_i^0 \) and \( \psi_i \) respectively are the continuum one-electron wave functions before and after introducing the molecule. \( \epsilon_{\text{xc}}[n] \) is the exchange-correlation energy density, calculated in the local-density approximation (LDA).\(^{25}\) The first two lines of Eq. (18) represent the kinetic-energy contribution to the energy difference, the third line is the exchange-correlation contribution, and the fourth and last line is the electrostatic term.

The electronic density \( n_{\text{mol}}(r) \) and the electronic energy \( E_{\text{mol}} \) of the isolated molecule are calculated within the same density-functional framework. The electronic density and the one-electron effective potential are also expanded in terms of Legendre polynomials up to the same limiting value \( \nu_{\text{max}} \). The \( l_{\text{max}} \) of the wave-function expansion [Eq. (4)] is the same as the one used in the molecule-jellium problem. The only difference is that only the one-electron bound states giving the isolated-molecule ground state are now filled.

The numerical solution of the present problem requires a truncation of the potential expansion at \( \nu_{\text{max}} \). However, the
Coulomb singularity at the nuclei is only reproduced by an infinite sum. The limitation in the number of components leads to a slight misrepresentation of the total electronic density at very short distances from the nuclei. Fortunately, the high $\nu$ components of the effective potential that we are neglecting are very close when the molecule is isolated and when the molecule is embedded in a jellium. As the magnitudes we are mainly interested in are the embedding energy $E_{\text{emb}}$ and the electronic density difference $\Delta n(r)$, which are differences between the molecule-in-jellium results and the isolated molecule results, the problem is overcome by solving both systems at the same level of approximation, i.e., with the same limiting value $r_{\text{max}}$. The possible inaccuracy of our results, due to the incorrect representation of the spatial regions close to the nuclei, is cancelled after substraction of the corresponding magnitudes. The convergence of $E_{\text{emb}}$ and $\Delta n(r)$ when increasing the number of $\nu$-components supports this argument. Typical values used in this work are $r_{\text{max}} = 6$ and $l_{\text{max}} = 8$.

The last point of our theoretical description deals with the modification in the continuum density of levels introduced by the molecule. The induced density of levels $\Delta \rho(k)$ is defined by

$$\Delta \rho(k) = 2k^2 \int d\Omega_k \int d^3r [|\psi_i(r)|^2 - |\psi_0(r)|^2], \quad (19)$$

where spin degeneracy is taken into account. With this definition, $\Delta \rho(k)$ is a density in $k$ space and the total number of electrons induced in the continuum $N_e$ is

$$N_e = \int dk \Delta \rho(k). \quad (20)$$

Direct calculation of $\Delta \rho(k)$ by means of Eq. (19) introduces artificial oscillations in the dependence of $\Delta \rho(k)$ on $k$, because the numerical $r$ integration is performed over a finite region of space. Former work on this subject has tried to eliminate these oscillations by adding a so-called nonlocal correction term. This correction works well for spherically symmetric potentials, but it has not been extended to non-spherical potentials.

In this paper, we overcome the problem by using the asymptotic behavior of the continuum wave functions to determine $\Delta \rho(k)$. For each value of the quantum number $m$ and the momentum $k$, we define a matrix $S^m(k)$

$$S^m(k) = [A^m(k) + iB^m(k)][A^m(k) - iB^m(k)]^{-1}, \quad (21)$$

where the $A^m(k)$ and $B^m(k)$ matrix is built from the coefficients that determine the asymptotic behavior of the $u^{(j)}_{lm}(r)$ wave functions

$$u^{(j)}_{lm}(r) \rightarrow A^{(j)}_{lm}(k)\sin(kr - l\pi/2) + B^{(j)}_{lm}(k)\cos(kr - l\pi/2). \quad (22)$$

The $S^m$ matrix is a unitary matrix that contains all the information about the scattering characteristics. The induced density of levels can be obtained from it by

$$\Delta \rho(k) = \frac{i}{\pi} \sum_m \text{Tr} \left[ \frac{dS^m}{dk} \right]^1 S^m, \quad (23)$$

where $\text{Tr}$ stands for the trace of the matrix.

To simplify this equation, we define the Hermitian matrix $D^m$ by

$$S^m = \exp[2iD^m]. \quad (24)$$

After some algebra, one can show that

$$\Delta \rho(k) = \frac{2}{\pi} \sum_m \text{Tr} \left[ \frac{dD^m}{dk} \right]. \quad (25)$$

Even if the identification of $\Delta \rho(k)$ with the excitation spectrum of the system is not rigorously founded in Kohn-Sham theory, we consider that this quantity is useful to better understand the screening of the embedded molecule. We use the decomposition of $\Delta \rho(k)$ into different $m$ components to explain the spatial distribution of the continuum electrons.

III. H$_2$ MOLECULE

The present Section is dedicated to the study of the H$_2$/jellium system. The H$_2$ molecule is very appealing for many reasons. Being the simplest molecule, the results are easier to interpret. In addition, it is one of the most used molecules in experimental studies on adsorption and dissociation at surfaces. Lastly, the H$_2$ molecule is a nonpolarized homonuclear molecule, with a different behavior from the LiH molecule, later presented.

Earlier calculations (except those of Ref. 19) on the H$_2$ molecule were performed with $l_{\text{max}} = 2$ and made use of a basis expansion for the wave function with variationally optimized parameters. Furthermore, the density of states could not be accurately derived for the reason explained in Sec. II. By contrast, our numerical solution of the Kohn-Sham equations allows to control the accuracy of our results in a systematic way and leads to a correct determination of the density of states.

Having in mind that, in a very simple picture, the approach of a molecule to a metal surface can be represented by the embedding of the molecule in a jellium of increasing electronic density $n_0$, we represent in Fig. 1 the electronic density difference $\Delta n(r)$, defined by Eq. (15), along the axis of the H$_2$ molecule, for different values of the jellium electronic density parameter $r_s$. The internuclear distance is set to the equilibrium distance of the isolated H$_2$ molecule ($d_{eq} = 1.40$ a.u.). Two effects are superimposed in the interaction between the molecule and the jellium. In general terms, the electronic density at the position of the H nuclei is largely increased when the jellium density increases. On the other hand, the electronic density at the midpoint between the two nuclei depletes, the hole being deeper as $r_s$ decreases. Both effects are indicating that the molecular bond weakens as the electronic density of the environment increases.

In previous works, it was claimed that the depletion of electronic density between the two centers of the molecule arises from the progressive filling of the first antibonding orbital of the molecule as the electronic density of the medium increases. To clarify this point, we plot in Fig. 2 the induced density of levels $\Delta \rho(k)$ for a H$_2$ molecule embedded in a jellium of $r_s = 2.0$, as well as the contribution to it coming from different values of the quantum number $m$. For convenience, we plot the density of levels defined by a
differential in \( k \) [see Eq. (20)] to avoid the divergence that appears at low energies for \( \sigma \) components when it is defined as a differential in energy.\(^{11}\)

Figure 2 shows that the screening of the H\(_2\) molecule is mainly produced by the continuum electrons of \( \sigma \) \((m=0)\) and \( \pi \) \((|m|=1)\) symmetries, with energies close to the Fermi level. In Fig. 2, we have also separated one of the contributions to the \( \sigma \) screening, \( \sigma_1 \), which is usually identified with the merging of the first antibonding state into the continuum.\(^{18,20,21}\) The separation of this component is not evident at all, as long as the \( \sigma \) continuum states are a linear combination of wave functions with different \( l \) symmetries \((l\) being the angular-momentum quantum number). Our procedure has been to select the \( \sigma \) components that would present a \( p \)-symmetry \((l=1)\) in the limit of very small internuclear distances (where spherical symmetry is recovered). After diagonalization of the \( D^{m=0} \) matrix, we obtain \((l_{\text{max}}+1)\) eigenvalues \( \delta_l(k) \). Following the adiabatic evolution of \( \delta_l(k) \) as the internuclear distance \( d \) goes to zero, we end up with the atomic limit, in which each of the \( \delta_l(k) \) eigenvalues corresponds to the phase-shift \( \delta_l(k) \) of a radial wave function with a well-defined value of the angular momentum \( l \). The line labeled as \( \sigma_1 \) in Fig. 2 is calculated by introducing in Eq. (25) only the eigenvalue \( \delta_l(k) \), which tends to \( \delta_{l-1}(k) \) when \( d \) tends to zero.

The \( \sigma_1 \) contribution shows a clear bump close to the Fermi level. We show in Fig. 3 its behavior as a function of the electronic density of the jellium. Hjelmberg \textit{et al.}\(^{20}\) and Johansson\(^{21}\) have explained the evolution of the antibonding component by considering it a resonant state in the continuum. The first antibonding state of the H\(_2\) molecule, the \( 2\sigma \) \textit{ungerade} state, would correspond to a delta function in the energy variable when the H\(_2\) molecule is isolated. The embedding of the molecule in the jellium couples the \( 2\sigma \) state with the continuum states of similar energies. As the electronic density of the environment increases, the resonance width is larger and its maximum goes below the Fermi level.

Anyhow, we consider that the problem is oversimplified if all the screening is explained in terms of this component. As we are treating a many-body system, it would be more adequate to say that the continuum density partially adopts a \( \sigma_1 \) character. In addition, we remark that the continuum \( \pi \) electrons also play an important role, their contribution to \( \Delta \rho(k) \) being of the same magnitude as that of the \( \sigma_1 \) component. Together with the \( \sigma_1 \) component, we plot in Fig. 3 the dominant contribution to the \( \pi \)-screening, denoted \( \pi_1 \), and calculated following the same adiabatic procedure used for \( \sigma_1 \): the \( \pi_1 \) contribution corresponds to the eigenvalue \( \delta_{l-1}(k) \) of the \( D^{m=-1} \) matrix, in the limit of very small internuclear distances. In this limit, \( \pi_1 \) would be the contribution to the screening made by the continuum \( p \) electrons with a nonzero value of \( m \). Figure 3 shows that the evolution of \( \pi_1 \) is quite similar to the evolution of \( \sigma_1 \): a peak close to the Fermi level that broadens and fills as the electronic density of the medium increases. We can conclude that the interaction between the molecule and the jellium cannot be explained only in terms of the \( \sigma_1 \) resonance. The continuum \( \pi \) electrons also play a fundamental role in the interaction.

The density of levels \( \Delta \rho(k) \) induced by the H\(_2\) molecule in the jellium is very similar to the density of levels induced by a He atom. Furthermore, the sum of the \( \sigma_1 \) and \( \pi_1 \) contributions to \( \Delta \rho(k) \) in the case of H\(_2\) is roughly the same as the \( p \) \((l=1)\) contribution to \( \Delta \rho(k) \) induced by the He atom. This similarity indicates that the role of the \( \sigma_1 \) and \( \pi_1 \) electrons in the H\(_2\) screening is quite similar to the role of the \( p \) electrons in the He screening.

Further information can be obtained from the embedding energy. We present in Fig. 4 the embedding energy \( E_{\text{emb}} \) for a H\(_2\) molecule as a function of the electronic density of the jellium. Our results agree with those of Ref. 18 and Ref. 19. We also plot in Fig. 4 the \( E_{\text{emb}} \) results for two isolated embedded H atoms (the limit of the molecular calculation for infinite internuclear distances), hence, the difference between both curves is the bonding energy of the H\(_2\) molecule. Our embedding energies for the H atom agree with those of Ref. 11. The zero of energy corresponds to the electronic energy of two isolated H atoms in the vacuum so that for \((n_0=0)\),

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the H₂ bonding energy in the vacuum (≈4.75 eV) is recovered.

For \( d = d_{eq} \) the embedding energy increases with increasing density in a nearly linear way: the large gain in kinetic energy, due to the stronger localization of the continuum electrons around the H nuclei, is not compensated by the decrease in the electrostatic and exchange-correlation terms.

The same tendency was observed in the case of embedded noble gas atoms, such as He, Ne, and Ar (Ref. 11). In fact, the slope of \( E_{emb} \) as a function of \( n_0 \) is very close for H₂ and He, which shows the weak reactivity of H₂ in the presence of any electronic environment. As a consequence, if one only accounts for the effects associated with the free electrons, the approach of H₂ to a surface should always cost energy.

For \( d > d_{eq} \) we observe a smooth transition from the curve corresponding to \( d > d_{eq} \) to that corresponding to infinite \( d \). We have plotted in Fig. 4 one intermediate case: \( d = 2d_{eq} \). For \( n_0 > 0.025 \) a.u., the embedding energy of the H₂ molecule with \( d = 2d_{eq} \) is very close to the embedding energy of two embedded H atoms and the molecule can be considered as dissociated. Some conclusions can be extracted from this plot. First, the bonding energy of a H₂ molecule is reduced when embedding the molecule in a jellium. Second, the absolute minimum is for H₂ in the vacuum. Furthermore, we can find some local minima of large \( d \) and small electronic densities \( n_0 \). A local minimum is also found for the infinite-distance limit, i.e., two isolated H atoms embedded in a jellium of electronic density \( n_0 \approx 0.0026 \) a.u. These features can be connected to the adsorption mechanisms of the H₂ molecule on a metal surface: H₂ molecules chemisorb dissociatively on free-electron-like surfaces and also on Cu, Ag, and Au after crossing of an activation barrier. Though the height of the barrier depends on molecular orientation, incidence angle, vibrational and rotational state, etc., its existence is clearly related to the positive slope of the embedding energy curve as a function of the density.

**IV. LiH MOLECULE**

This section is dedicated to the description of the embedding of a LiH molecule in a jellium. Two main features have driven our interest towards the LiH molecule. Firstly, it is a simple heteronuclear molecule and, secondly, the isolated LiH molecule has a dipole moment of \( \mu \approx 2.31 \) a.u., the negative pole centered on the H atom. We are interested in the characterization of the metallic medium response when the embedded molecule presents a dipole moment. The iso-
The quantification of these effects is presented in Fig. 6, in which we plot the electric dipole moment of both the bound and continuum components of the induced electronic density as a function of the jellium electronic density \( n_0 \). In the case of the bound dipole moment, the plotted quantity is the difference between the electronic bound dipole moment of the embedded molecule and that of the isolated molecule.

The density of levels \( \Delta \rho(k) \) induced by a LiH molecule in the continuum is quite different from the \( \Delta \rho(k) \) induced by a \( \text{H}_2 \) molecule. The continuum density adopts a strong dipole moment of the whole system \( \mu^{\text{tot}} \) is composed by three terms

\[
\mu^{\text{tot}} = \mu^{\text{bound}} + \mu^{\text{cont}} + \mu^{\text{nucl}},
\]

where \( \mu^{\text{bound}} \) is the dipole moment of the bound density, \( \mu^{\text{cont}} \) is the dipole moment of the continuum states, and \( \mu^{\text{nucl}} \) is the dipole moment of the nuclei. In the case of the bound component, the quantity \( \Delta \mu^{\text{bound}} \) plotted in Fig. 6 is the difference between \( \mu^{\text{bound}} \) in the embedded molecule and \( \mu^{\text{bound}} \) in the isolated molecule.

The electronic density around the embedded molecule not only screens the Coulomb potential of the bare nuclei, but also the dipolar term of the potential at long distances. In other words, the continuum electrons are polarized to compensate the dipole moment of both the bound density and the nuclei \( (\mu^{\text{cont}} = -\mu^{\text{bound}} - \mu^{\text{nucl}}) \). Figure 6 shows that, when the electronic density of the medium increases, the bound dipole moment \( \mu^{\text{bound}} \) and the continuum dipole moment \( \mu^{\text{cont}} \) are modified in the opposite sense, the sum of both always compensating the dipole moment of the nuclei \( \mu^{\text{nucl}} \approx 3.01 \text{ a.u.} \). For small values of the background electronic density \( (r_s < 6) \), the distance at which the molecule dipole is totally screened is quite large \( (r_s > 20 \text{ a.u.}) \) and numerical convergence is difficult to achieve. For this reason, \( \mu^{\text{cont}} \) is only plotted for \( r_s = 6 \text{ a.u.} \).

The density of levels \( \Delta \rho(k) \) induced by a LiH molecule in the continuum is quite different from the \( \Delta \rho(k) \) induced by a \( \text{H}_2 \) molecule. The continuum density adopts a strong \( \pi \) character. This is shown in Fig. 7 in which we plot, as an
example, the density of levels induced in the continuum \( \Delta \rho(k) \) for a LiH molecule in a free electron gas of \( r_s = 4.0 \). We also represent the \( \sigma \), \( \pi \), and \( \sigma_1 \) contributions to \( \Delta \rho(k) \). The latter is calculated using the same procedure as in the preceding section. Figure 7 shows that most of the screening is performed by \( \pi \) electrons close to the Fermi level. We have checked that the \( \pi \) electron density is mainly placed at the vicinity of the Li atom, in the plane perpendicular to the molecular axis. For smaller values of \( r_s \), the \( \sigma \) component of \( \Delta \rho(k) \) becomes more negative, due to the closeness of the \( 2\sigma \) bound state to the bottom of the band. For \( r_s < 2.0 \), the energy of the \( 2\sigma \) state merges into the continuum and becomes a resonance. As a consequence, the \( \sigma \)-induced density of levels changes its sign, presenting a large positive peak close to the bottom of the band. The change of sign of the low-energy-induced density of levels in the continuum when one of the bound states disappears is a general property.27

The shape of the induced density of levels in the case of the embedded LiH molecule is very similar to the sum of the density of levels independently induced by an embedded Li atom and an embedded H atom. This is again a consequence of the displacement of bound charge from the Li atom to the H atom. The continuum electrons have to screen a molecule that is, roughly speaking, a combination of a \( \text{H}_2^+ \) ion (the ground state of an embedded H atom when \( r_s > 2.0 \)) and a \( \text{Li}_1^+ \) ion (the ground state of the embedded Li atom when \( r_s < 6.5 \)).

We plot in Fig. 8 the evolution of the \( \sigma_1 \) and \( \pi_1 \) components of \( \Delta \rho(k) \) as the electronic density of the medium increases. The sum of both contributions roughly equals the total \( \Delta \rho(k) \) for values of \( k \) below the Fermi level. In comparison with the \( \text{H}_2 \) case (Fig. 3), the \( \sigma_1 \) curve presents much more structure, with two clear bumps. The first of them is already filled for \( r_s = 6.0 \) and broadens as \( r_s \) decreases. The second one lies always above the Fermi level and does not intervene in the screening process for all values of \( r_s \) considered in this work. On the other hand, the \( \pi_1 \) contribution shows a clear peak close to the Fermi level. This peak is being filled as \( n_0 \) increases.

The analysis of the induced electronic density around the LiH molecule and the study of the embedding energy curves (later presented) show that the bonding of the LiH molecule is weakened when increasing \( n_0 \). Figure 8 shows that this weakening cannot be explained by the filling of a \( \sigma_1 \) resonance (corresponding to the first excited state of the isolated LiH molecule). The weakening of the molecular bonding is the result of a complex screening process, due to the whole electronic density of the medium. In the case of the LiH...
molecule, Fig. 8 shows that the electronic density induced in the continuum has mainly a $\pi_1$ character.

Regarding the energy problem, the LiH molecule is a good example of a quite different situation compared to the activated-dissociation adsorption of the H$_2$ molecule. We plot in Fig. 9 the embedding energy $E_{\text{emb}}$ for the LiH molecule, when the distance between the two nuclei is the isolated molecule equilibrium distance $d_{\text{eq}}$, as a function of the electronic density of the medium $n_0$.

For small $n_0$, the embedding energy of the LiH molecule has a negative slope, with a minimum at $n_0 \approx 6 \cdot 10^{-4}$ a.u. The existence of this minimum is an indication of the chemical reactivity of the LiH molecule: its coupling with an external electronic density diminishes the electronic energy of the whole system. The negative electrostatic energy provided by the rearrangement of the electronic density around the molecule compensates the increase of electronic kinetic energy, due to the stronger localization of the continuum states.

We also plot in Fig. 9 the infinite-distance asymptotic limit, i.e., the embedding energy of the isolated Li and H atoms. The embedding energy for intermediate internuclear distances follows a smooth transition between the two lines. The difference between these two lines represents the bonding energy of the embedded LiH molecule as a function of the electronic density of the medium, for a fixed value of the internuclear distance $d_{\text{eq}}$. The decrease of the bonding energy as $n_0$ increases shows that, as was the case for H$_2$, one of the effects of the screening created by the medium electrons is to weaken the bonding of the molecule. This feature shows the complexity of the bonding problem when the molecule is attached to an electronic environment: even if there is a transfer of electronic charge between the two centers of the molecule, the bonding energy decreases.

The difference between the LiH curve and the separated atom limit also shows that the energy of the embedded molecule is lower than the energy of the isolated atoms for $n_0 < 0.013$ a.u. The absolute minimum of the plot corresponds to an embedded LiH molecule. This means that in the interaction between a LiH molecule and an external electronic environment, the molecule could find an energy minimum when it is embedded without being dissociated. In terms of molecule/surface interactions, this picture would correspond to molecular adsorption.

When embedding isolated atoms in a jellium, the deepness and position of this kind of minima can be related to adsorption energies and distances. In fact, the results are not qualitatively different if the host is an homogeneous jellium or a jellium surface. In a simple picture, the electronic density at which the atom finds the embedding energy minimum determines the distance from the surface at which the atom adsorbs. In the case of a diatomic molecule, the situation is not so simple, as the geometry of the problem is quite more complicated. But, in any case, the embedding model offers a qualitative description of the adsorption process.

V. CONCLUSIONS

In this paper, we have used the embedding approach to describe the interaction between a diatomic molecule and a metal surface. By using density-functional theory, we have obtained self consistently the embedding energy and the electronic density induced by the molecule in the jellium. Both quantities are useful tools to understand the screening caused by the jellium electrons between the two centers of the molecule. Our method is parameter-free (no need of any basis-set) and general (any diatom). It allows the determination of the density of states through the asymptotic properties of the Kohn-Sham orbitals. Furthermore the accuracy of the results may be checked in a systematic way.

We have presented results for H$_2$ and LiH. In general terms, we have shown that the molecular bond is weakened when the molecule is embedded. In the case of H$_2$, the interaction between the molecule and the jellium cannot be explained only in terms of the first antibonding resonance. The continuum $\pi$ electrons also play an important role. The behavior of the embedding energy as a function of the jellium electronic density shows that the interaction of H$_2$ with a jellium is quite similar to that of a closed-shell atom, such as He. A local electron minimum is only found after dissociation of the H$_2$ molecule.

The embedding of a polar molecule such as the LiH molecule gives rise to the polarization of the host. The self-consistent calculation of the electronic density shows that the jellium enhances the transfer of bound charge between the two centers of the molecule, thus increasing the dipolar moment of the bound density. Accordingly, the density of levels has a strong similarity with that of an embedded pair of H$^-$ and Li$^+$ ions. We have shown that $\pi$ electrons play an important role in the screening process, which confirms that the interaction of a molecule with an external electronic density cannot be described simply in terms of the population of the lowest unoccupied orbital of the isolated molecule. Finally, our calculations point to the possibility of molecular adsorption of LiH, though with a weaker bond than in vacuum. Hence, nonpolar and polar molecules show a qualitatively different behavior when embedded in a jellium.

The formalism used in the present paper has the virtue of flexibility: the sensitivity of the final results to parameters-
such as the internuclear distance, the jellium electronic density, or the nuclear charges is easily quantified. Furthermore, the characterization of the physical processes involved in the interaction is quite direct. In this respect, the embedding approach is a useful complement to results obtained from \textit{ab initio} calculations, accounting for a more sophisticated representation of the surface electronic structure.

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