

Ground state of a hydrogen ion molecule
immersed in an inhomogeneous electron gas

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Abstract

In this work we have calculated the ground state energy of the hydrogen molecule, H_2^+ , immersed in the highly inhomogeneous electron gas around a metallic surface within the local density approximation. The molecule is perturbed by the electron density of a crystalline surface of Au $\langle 100 \rangle$ with the inter-nuclear axis parallel to the surface. The surface spatial electron density is calculated through a Linearized Band Structure Method (LMTO-DFT). The ground state of the molecule-ion was calculated using the Born-Oppenheimer approximation for a fixed-ion while the screening effects of the inhomogeneous electron gas are depicted by a Thomas-Fermi like electrostatic potential. We found that within our model the molecular ion dissociates at the critical distance of 2.35 a.u. from the first atomic layer of the solid.

Introduction

The interaction of swift molecules with solid surfaces has been studied with increasing interest during the last two decades [1-15]. The interaction behavior at high velocities [6-11] has been confirmed using small molecular ions, although there are several questions still open. On the other hand, in the low velocity range [12-15] the influence of various mechanisms such as dissociation [4, 5, 14], recombination [3, 12, 15] and non-linear quantum effects [1, 2, 13] should be clarified.

When a H_2^+ molecular ion collides with a metallic surface it may dissociate into two fragments. Afterwards, the resulting fragments begin to separate by the influence of the Coulomb repulsion, becoming far apart in a few femtoseconds. This phenomenon is the so called ‘‘Coulomb explosion’’. The molecular fragments move inside the solid affected by their mutual repulsion, their interaction with the bulk atoms and also losing energy through electronic excitations of the medium. In the low velocity range only the electron hole excitations are important. It is well known that the fragments emerge with a low probability of recombination giving a poor yield of exiting molecules [3, 12, 15].

The knowledge of both the ground state energy and the internuclear distance of the molecule components close to the surface, allows in a first approximation to determine the conditions for both dissociation and recombination of the fragments at the entrance and the exit of the solid respectively [16]. The electronic density of the surface is inhomogeneous and it is modeled within the local density approximation (LDA).

In this work we will be focused in determining both the ground state energy E and the internuclear distance R of a hydrogen molecular ion as a function of the distance D to the surface, where D is measured along the $\langle 100 \rangle$ direction. We consider the fixed ion approximation with the molecular axis parallel to the surface’s solid although we comment at the end how our method could be generalized to different molecular orientations and to diverse surfaces of the crystalline solid. Atomic units are used throughout the work ($m_e = e = \hbar = 1$).

Method

Let us start by defining the Hamiltonian for the molecular ion immersed in the inhomogeneous electron gas at the surface,

$$H_{\text{Molecular-ion}} = -\frac{\nabla_e^2}{2} - \frac{\nabla_A^2}{2m_p} - \frac{\nabla_B^2}{2m_p} - V(r_A) - V(r_B) + V(R) \quad (1)$$

where $V(r_A)$ and $V(r_B)$ are the interaction potentials between the bound electron and each nuclei while $V(R)$ represents the interaction potential between the nuclei themselves. Subscripts A and B represent the nuclei with mass m_p . All these interaction potentials include the effects of the inhomogeneous electron gas through the use of screening parameters which are obtained self-consistently, as described later.

In our procedure we obtain first the electronic density of the unperturbed surface. Afterwards, we obtain the ground state energy by solving the Schrodinger equation for the

molecular ion, embedded with its axis parallel to the crystal surface, in the inhomogeneous electron gas of the surface region (figure 1). The effect of the medium is contained in the screening parameters which are obtained independently by using a self-consistent method based on the Friedel's sum rule.

In order to describe the electronic density of surface and bulk in real space retaining their inhomogeneities, we have performed detailed calculations for the Au <100> system. Our description is based on the ab initio LMTO (linear muffin-tin orbitals) method which has been explained elsewhere [17, 18]. The method is based on DFT (density functional theory) within the LDA (local density approximation) for the exchange correlation potential. The calculation solves iteratively the Kohn-Sham equations, taking into account the spatial environment of the atoms, until self consistency is reached. The charge densities using this method are in excellent agreement with those obtained from a linear augmented plane-wave (LAPW) full-potential calculation, although LMTO considers an atomic sphere approximation for the one electron potential and empty spheres to simulate the interstitial region in open structures [18]. To model the crystalline surface of Au (100) we have used a rectangular supercell, in which we fill a portion of space with the so called "empty atoms", and then straightforwardly calculate the charge density distribution as a function of width in the empty region. When the charge density distribution does not change along the direction in which the width of the supercell grows, then we are sure that we have reached the surface. At this point, some care has to be done with the width of the metallic slab to be sure that it has metallic character. These electronic density calculations do not take into account the reconstruction of the Au-surface.

We are interested in the study of the ground state of the molecule moving at low energy (1 keV) and immersed in the inhomogeneous electron gas of the metal surface with the aid of a variational method in the Born-Oppenheimer approximation. However, since the characteristic velocity of electrons in metals is much larger than that of a hydrogen molecule with energy of the order of 1 keV, we use the static approximation, i.e. the protons screened by electrons from the metal are considered to be at rest [14].

The description of the perturbed intra-molecular interactions in the ion, which includes the effect of the inhomogeneous electron gas, considers the use of the hydrogen-like screened potentials,

$$V_{\text{Interaction}} = \frac{1}{r} \times (1 + \beta) e^{-2\beta r} \quad (2)$$

In equation (2), β is the screening parameter which is a function of the local electron gas

density. If $\beta = 0$ we recover the bare Coulomb interaction. This parameter is calculated by solving the Schrödinger equation through a self-consistent way in which the Friedel's sum rule [19, 20] must be satisfied (figure 2.)

Within the Born-Oppenheimer approximation the Hamiltonian gets reduced to

$$H_{\text{Molecular-ion}} = -\frac{\nabla_e^2}{2} - V(r_A) - V(r_B) + V(R) \quad (3)$$

The corresponding Schrödinger equation of our system, is:

$$\left\{ -\frac{\nabla_e^2}{2} - V(r_A) - V(r_B) + V(R) \right\} \Psi = E\Psi. \quad (4)$$

We expand the wave function of the molecule through a linear combination of atomic orbitals (LCAO) [21, 22, 23]

$$\Psi = \sum_i c_i \varphi_i. \quad (5)$$

In our case, we have considered the 4s2p basis set. The coefficients c_i are parameters to be calculated. The optimum values of the coefficients we are referring to, are found by application of the variational method, which means that we have to solve the secular equations,

$$\sum_i c_i (H_{ij} - ES_{ij}) = 0 \quad (6)$$

Here, $S_{ij} \equiv \int \varphi_i \varphi_j d\tau$, and $H_{ij} \equiv \int \varphi_i H \varphi_j d\tau$. After solving the secular equations (6), we obtain the molecular potential energy as a function of the internuclear distance R . The minimum of this curve represents the equilibrium value for the ground state energy of the molecule immersed in the inhomogeneous electron gas.

Results and Discussion

In Figure 2 we have plotted the screening parameter β , consistent with the Friedel's sum rule, as a function of the electronic density, characterized by the parameter r_s . As expected for larger densities (smaller values of r_s) the screening parameter gets larger. Figure 3 shows a profile of the mean electronic density as a function of the ion-surface distance D . This average is obtained using the calculated three-dimensional electronic density for the $\langle 100 \rangle$ direction of monocrystalline gold. In Figure 4 we show the molecular potential energy E as a function of R for several values of the screening parameter β . For larger values of the β parameter the shallowness of the potential well gets lower until it vanishes when $\beta = \beta_c = 0.86$ a.u.. It is also

clear that the internuclear distance R_{\min} (at which the potential energy E for the molecular ion has a minimum) gets larger for larger values of β . This is shown in Figure 5 where R_{\min} is drawn as a function of the screening parameter β . We see that R_{\min} changes slowly for β values less than 0.6 a.u. and it increases quickly for values close to β_c . This result agrees qualitatively with the results of Ref. [5]. We shall interpret the zero value of the potential energy E as the condition for the dissociation of the molecular ion, characterized by β_c .

Before proceeding further we note that for each \mathbf{r} there is a value of the electronic density $\rho(\mathbf{r})$ to which we can (in the LDA) relate the electron gas parameter r_s through the relationship,

$$\rho = \left(\frac{4\pi}{3} r_s^3 \right)^{-1} \quad (7)$$

With the information contained in Figures 2 and 3 plus equation (7) it is straightforward to obtain the ion-surface distance at which the molecular ion dissociates (D_c). We do that as follows: with the critical screening parameter $\beta_c = 0.86$ a.u., we obtain (through figure 2) the corresponding critical values for $r_s = 2.45$ a.u. which by equation (7) yields $\rho = 0.016$ a.u.. Finally, this value of ρ and consideration of figure 3 allows us to obtain the corresponding value for the critical distance to the first atomic layer $D_c = 2.35$ a.u.. Therefore, for any value less than D_c the molecular system does not accept bound states (for the model under consideration which assumes that the velocity of the molecular ion is much smaller than the Fermi velocity of the electrons of the solid).

This model can be generalized for different surfaces of crystalline solids. We must remember that the method LMTO is valid if we can build a rectangular supercell, in which we fill a portion of space with a crystalline structure and the other portion with the so called "empty atoms". On the other hand, the effect of the orientation of the molecular ion, in this model, can be taken into account by consideration of a different screening for each one of the nuclei that form the molecule, which makes it possible to calculate the ground state of the molecular ion applying the same method with two or more screening parameters.

Conclusion

Within a simple model we have calculated the equilibrium-energy and the corresponding internuclear distance for the H_2^+ molecular ion near a metallic surface; our procedure has been applied to a wide range of values of the screening parameter. This parameter is connected with

the dimmer-surface distance and it allows us to determine, within the approximations of our model, the critical distance to the surface where the molecular ion gets dissociated.

Analyzing our results we are able to say that the molecule dissociation takes place before reaching the first atomic layer of the solid, i.e. the molecule will not survive inside the solid. However, by consideration of the dynamic of the processes one can expect that under special conditions the fragments can recombine at the exit of the near surface of the solid foil.

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Captions

Figure 1. Schematic representation of a hydrogen molecule-ion near a mono-crystalline surface Au(100). The dimmer axis is parallel to the solid's surface. The dashed line represents the mean electronic density (ρ) of the target surface, R is the internuclear distance and D is the distance between the ion and the first atomic layer. A , B and e correspond to the two protons and the electron respectively.

Figure 2. The screening parameter β calculated through a self-consistent method, as a function of r_s . (The line is a just a fit to guide the eye)

Figure 3. Electronic density ρ at the surface region as a function of the distance to the first atomic layer D . The symbols correspond to the present calculations, and the continue line is just a fit to guide the eye.

Figure 4. Relationship between the potential energy of the hydrogen molecule-ion and the internuclear distance R for different screening values.

Figure 5. Dependence between the internuclear distance R_{\min} (at which the potential energy E gets a minimum) and the screening parameter β . (The line is a fit to guide the eye.)









