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# THE INTERACTION OF $H_2$ WITH A JELLIUM SURFACE

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We calculate the interaction between a $H_2$ molecule and a metal surface, represented by $r_s = 2$ jellium, using the Gordon–Kim method. The adsorption curves for $H_2$ parallel and perpendicular to the surface are presented, and analyzed using an independent-atom effective potential. The molecular potential curve for $H_2$ near the surface is also analyzed.

## 1. Introduction

The interaction of molecules with a metal surface has been studied theoretically by a number of authors in a variety of models. There have been semi-empirical quantum mechanical calculations of small molecules near a cluster of metal atoms [1], ab initio studies of a small number of metal atoms and a diatom [2], calculations with model hamiltonians [3], and calculations of the large intermolecular or interatomic distance portion of the potential curve for diatomic molecules near a metal surface modelled as a continuum [4–7]. These studies are concerned mainly with the breaking of the molecular bond as the diatom approaches the surface, that is, the dissociative adsorption of a diatomic molecule. However, since the exact solution of this problem is unfeasible, the various methods are used for that part of the problem (or for that model) for which they are most suited. For example, the calculations by Sinanoğlu and Pitzer [4], MacLachlan [5], and Mahanty and March [6] are concerned with the attractive part of the molecular potential curve when the molecule is reasonably near the surface but outside the spill-out region of the metallic electrons. Using image theory or second order perturbation theory, these authors compute the *additional* interaction between the atoms in a diatomic for large interatomic distance, $R$, due to the presence of the metal surface. This additional term can be considered as due to the interaction of the fluctuating charge density on one atom with the *image* of the fluctuating charge density of the other atom. These authors found that when the diatomic bond is perpendicular to the metal surface, this additional term is attractive, while when the bond is parallel to the surface, this term is repulsive. This result led these authors to speculate (by extrapolation to values of $R$ close to the equilibrium distance) that the diatomic bond is weakened if the molecule is parallel to the surface and strengthened when it is perpendicular to the surface. It is clear that because this result refers only to the large $R$ part of the curve, other effects at small $R$ may overwhelm it. A more careful study of the molecular potential curve near $R_{eq}$, the equilibrium bond distance, when the molecule is near the surface is clearly necessary. Other work [6,7] on the diatomic potential for the molecule very close to the metal has been done, but it is also for large $R$.

In this paper, we present a calculation of the interaction of a hydrogen molecule near a metal surface as a function of the distance, $d_{c.m.}$, of the center of mass of the molecule to the metal surface, the interatomic distance (i.e. bond distance), $R$, and the orientation of the molecule to the surface (parallel or perpendicular). Since $H_2$ is a closed shell system, the interaction of it with a metal surface, at fixed $R$, should resemble that of an inert gas atom with the metal. The latter problem

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has been treated by Landman and Kleiman [8], Zaremba and Kohn [9] and van Himbergen and Silbey [10]. The last-named paper uses the Gordon–Kim [11] procedure which has proved to be so useful in atom–atom interaction calculations [12].

The paper is laid out as follows: in section 2, we present the model used and discuss the notation; in section 3, the results for the adsorption curves for fixed $R$ and orientation are presented and compared to an alternative model based on effective atom surface interactions. In section 4 the molecular potential (i.e. the interaction for fixed $d_{\mathrm{c.m.}}$ and varying $R$) curves for a few values of $d_{\mathrm{c.m.}}$ are presented and discussed. Section 5 is a summary of the results.

## 2. The model and Gordon–Kim method

We consider the interaction between $H_2$ and a metal, represented by a jellium model [13] as was done in treating the inert gas atom–metal interactions [10]. The Gordon–Kim (GK) method uses the density functional theorem of Hohenberg and Kohn [14] in an approximate form. The first approximation is that the electron density of the combined molecule–metal system is assumed to be the sum of the densities of the free molecule and the free metal. This approximation should be accurate for systems *not* forming a chemical bond (as in this case) where there is little rearrangement of the density. The second is the use of the homogeneous electron gas density functional in the calculation. This approximation is more problematical; the recent article by Clugston [12] discusses accuracy and the various revisions of the basic model which have been proposed in recent years.

In order to perform the GK calculation we need as the input the densities of the free $H_2$ molecule and the jellium surface. For the former, we took the densities found by Liu [15] which are as good as those computed by Kołos and Wolniewicz [16] and thus are the most accurate available densities. For the jellium surface, we took the self-consistent densities of Kohn and Lang [13], or since there is virtually no difference for the results of this calculation for $r_s = 2$ [10], the densities of Smith [17], which have a particularly simple analytic form.

## 3. Adsorption curves

### 3.1. Gordon–Kim results

The GK calculation gives potential curves at fixed internuclear separation for the parallel configuration, $U^{\parallel}(R,d) - U^{\parallel}(R,\infty)$ and the perpendicular configuration, $U^{\perp}(R,d) - U^{\perp}(R,\infty)$. In table 1, the numerical values of these calculations are given. In fig. 1, these curves are plotted for $R$ = 1.4 au (the equilibrium bond distance). There are a number of important points to be made. First, at large distances from the metal where attractive forces dominate, the hydrogen molecule has lower energy when perpendicular to the surface, while at small distances when repulsive forces

Table 1
Adsorption energies $[U(R,d) - U(R,\infty)]$ (in $\mathrm{cm}^{-1}$) calculated by Gordon–Kim method

| $R$ (Å) | $d$ = 1.5 Å | $d$ = 2.0 Å | $d$ = 2.5 Å | $d$ = 5 Å |
|---|---|---|---|---|
| parallel configuration | | | | |
| 0.42 | +268 | −152 | −164 | −4.7 |
| 0.53 | +206 | −202 | −195 | −5.7 |
| 0.63 | +136 | −255 | −228 | −6.7 |
| 0.74 | +59 | −309 | −261 | −7.8 |
| 0.85 | −17 | −366 | −296 | −9.0 |
| 1.06 | −162 | −472 | −364 | −11.4 |
| 1.59 | −465 | −689 | −496 | −16.4 |
| 2.12 | −630 | −792 | −553 | −18 |
| perpendicular configuration | | | | |
| 0.42 | 28970 | −100 | −149 | −4.9 |
| 0.53 | 30730 | −121 | −176 | −6.0 |
| 0.63 | 32262 | −142 | −205 | −7.3 |
| 0.74 | 33360 | −159 | −235 | −9.0 |
| 0.85 | 34457 | −169 | −266 | −11 |
| 1.06 | 36432 | −160 | −320 | −15 |
| 1.59 | 38846 | +79 | −413 | −29 |
| 2.12 | 39724 | +825 | −353 | −47 |

parallel and perpendicular configurations for $R$ = 0.74 Å, selected values of $d$

| $d$ (Å) | parallel | perpendicular |
|---|---|---|
| 1.7 | −185 | 134 |
| 1.9 | −292 | −103 |
| 2.1 | −316 | −208 |
| 2.3 | −298 | −241 |
| 3.0 | −159 | −164 |
| 3.5 | −83 | −91.3 |

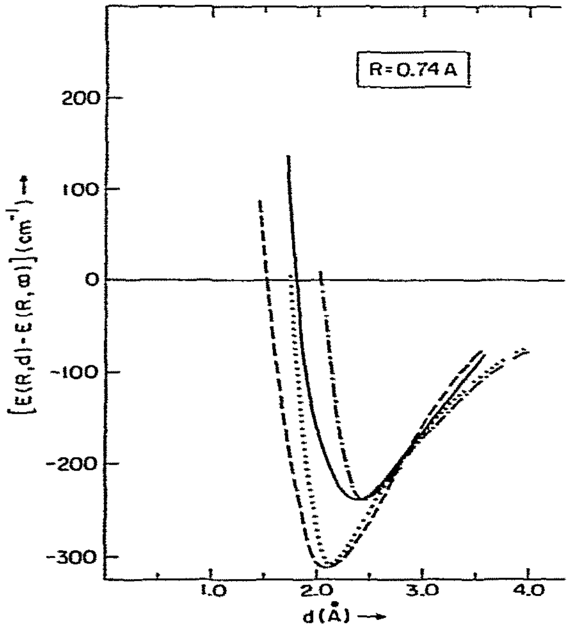

Fig. 1. $H_2$ adsorption energies for $R$ = 0.74 Å as a function of $d$. Solid curve: Gordon–Kim (GK) calculation for perpendicular orientation Dashed curve: GK calculation for parallel orientation. Dot-dash curve: independent atom (IA) calculation for perpendicular orientation. Dotted curve: IA calculation for parallel orientation.

dominate, the energy is lower when the molecule is parallel to the surface. We point out in the next section that this is a general characteristic of a large class of potentials. Second, the well depth is found to be approximately 300 $cm^{-1}$. An $r_s \approx 2$ jellium model approximates Al; however, there are no reliable experimental well depths for Al–$H_2$ in the literature. The scattering of $H_2$ from Ag surfaces ($r_s \approx 3.0$) has recently [18] been interpreted to lead to a well depth of between 50 and 300 $cm^{-1}$. Our (preliminary) calculations for $r_s = 3$ lead to a well of $\approx 300$ $cm^{-1}$, as in the case of $r_s = 2$. The large error bar in the experimental results is characteristic [19] of these measurements.

### 3.2. Independent effective atoms

If we consider $H_2$ as being made up of two independent effective atoms each interacting with the metal surface by a 9–3 potential, then we have

$$U(R,d_1,d_2) = \alpha/d_1^9 + \alpha/d_2^9 - \beta/d_1^3 - \beta/d_2^3\,, \qquad (1)$$

where we have labelled the perpendicular distance of atom $i$ to the surface as $d_i$, the repulsive parameter as $\alpha$, and the attractive parameter as $\beta(\alpha,\beta > 0)$. For molecules parallel to the surface, we find

$$U^{\parallel}(R,d) = 2(\alpha/d^9 - \beta/d^3)\,, \qquad (2)$$

while for the perpendicular configuration

$$U^{\perp}(R,d) = \alpha[(d+\tfrac{1}{2}R)^{-9} + (d-\tfrac{1}{2}R)^{-9}]$$
$$- \beta[(d+\tfrac{1}{2}R)^{-3} + (d-\tfrac{1}{2}R)^{-3}]\,, \qquad (3)$$

where $d$ is the center of mass distance of the surface. Note that in the attractive region, $U^{\perp} < U^{\parallel}$ and in the repulsive region $U^{\perp} > U^{\parallel}$, as in the GK results, and independent of the values of $\alpha$ and $\beta$ (as long as both are greater than zero). Values of $\alpha$ and $\beta$ consistent with the GK calculation can be found by fitting the minimum of the parallel configuration potential energy found by the GK using the form of eq. (2). Thus, $U^{\parallel}_{\min} = -316$ $cm^{-1}$ at $d = 2.1$ Å (for $R = 0.74$ Å). This leads to

$$\alpha = 6.3 \times 10^4\ \mathrm{cm}^{-1}\ \text{Å}^9 = 88.5\ \mathrm{au}\,, \qquad (4a)$$

$$\beta = 2.20 \times 10^3\ \mathrm{cm}^{-1}\ \text{Å}^3 = 0.068\ \mathrm{au}\,. \qquad (4b)$$

The potential curves found using these values are also plotted in fig. 1. Note that the well depths found in both methods agree very well although the repulsive wall is harder in the effective atom method than in the GK calculation. In addition, the GK method fails to give the van der Waals tail ($\propto d^{-3}$) for large $d$, although it does give a $d^{-3}$ part for a small range of $d$. Table 2 gives a summary of the results of the GK and independent atom calculations.

### 3.3. Calculation of the van der Waals attraction parameter

A simple variational calculation of the van der Waals parameter $\beta$ can be made following the work of Karplus et al. [20]. If the frequency dependent tensor polarizability of the molecule, $\boldsymbol{\alpha}(\omega)$, and the response function of the metal surface, $B(\omega)$, are known, then an exact calculation of the van der Waals coefficient can be made, since [5,9]

Table 2
Comparison of GK and independent atom results [a] ($R$ = 0.74 Å) for adsorption energies $[U(R,d) - U(R,\infty)]$ (in cm$^{-1}$)

| $d$ (Å) | Parallel | | Perpendicular | |
|---|---|---|---|---|
| | GK | IA | GK | IA |
| 1.5 | 59 | 1974 | 33360 | 19936 |
| 1.7 | −185 | 167 | 134 | 3745 |
| 1.9 | −292 | −251 | −103 | 608 |
| 2.0 | −309 | −303 | −159 | 129 |
| 2.1 | −316 | −316 | −198 | −99 |
| 2.3 | −298 | −292 | −241 | −242 |
| 2.5 | −261 | −249 | −235 | −246 |
| 3.0 | −159 | −156 | −164 | −167 |
| 3.5 | −83 | −101 | −91 | −107 |
| 5.0 | −7.8 | −35 | −9 | −36 |

[a] See text for values of $\alpha$ and $\beta$.

$$C = \mathrm{tr}\left[\frac{1}{2\pi}\int_0^\infty \mathrm{d}x\, \boldsymbol{\alpha}(\mathrm{i}x)\cdot \mathrm{B}(\mathrm{i}x)\right] . \tag{5}$$

The metal is modelled by a plasma continuum, so [9] with the $z$ direction perpendicular to the surface

$$\mathrm{B}(\omega) = \frac{1}{8}\left[\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right]\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 2\end{pmatrix} , \tag{6}$$

where

$$\epsilon(\omega) = 1 - \omega_\mathrm{p}^2/\omega^2 \tag{7}$$

and $\omega_\mathrm{p}$ is the plasma frequency, $\omega_\mathrm{p}^2 = 3(e^2/m)/r_\mathrm{s}^3$. Thus the frequency dependent term multiplying the matrix is given by

$$\tfrac{1}{8}\,\omega_\mathrm{p}^2/(2\omega^2 + \omega_\mathrm{p}^2) = \tfrac{1}{8}\,\omega_\mathrm{s}^2/(\omega^2 + \omega_\mathrm{s}^2) , \tag{8}$$

where $\omega_\mathrm{s} = 2^{-1/2}\omega_\mathrm{p}$ is the surface plasmon frequency. To calculate the approximate frequency dependent polarizability of $H_2$, we have used (i) a one-term variation function, taking the necessary matrix elements from the work of Kołos and Wolniewicz [16]:

$$\langle x_1^2 + x_1 x_2\rangle_\mathrm{KW} = 0.70659 \text{ au} , \tag{9a}$$

$$\langle z_1^2 + z_1 z_2\rangle_\mathrm{KW} = 0.8730 \text{ au} \tag{9b}$$

and (ii) a two-term form for $\alpha_\parallel$ and $\alpha_\perp$, using the moments given by Langhoff et al. [20].

The form of $\alpha_\perp(\omega)$ and $\alpha_\parallel(\omega)$ (i.e. perpendicular and parallel to the molecular axis) for $H_2$ is, in the one-term approximation,

$$\alpha_\perp(\omega) = \frac{2}{(4\langle x_1^2 + x_1 x_2\rangle^2)^{-1} - \omega^2} = \frac{2}{0.42 - \omega^2} \text{ au} , \tag{10a}$$

$$\alpha_\parallel(\omega) = \frac{2}{(4\langle z_1^2 + z_1 z_2\rangle^2)^{-1} - \omega^2} = \frac{2}{0.31 - \omega^2} \text{ au} . \tag{10b}$$

This implies effective excitation frequencies of $H_2$ of $\omega_\perp = 0.65$ au and $\omega_\parallel = 0.56$ au. The two term form for $\alpha_\perp$ and $\alpha_\parallel$ are (in au)

$$\alpha_\perp(\omega) = \frac{0.9295}{0.2581 - \omega^2} + \frac{1.0705}{1.0539 - \omega^2} , \tag{11a}$$

$$\alpha_\parallel(\omega) = \frac{1.2086}{0.2296 - \omega^2} + \frac{0.7914}{0.6713 - \omega^2} . \tag{11b}$$

We may now evaluate the van der Waals coefficient for the two orientations of the $H_2$. For $H_2$ parallel to the surface,

$$C^\parallel = \frac{1}{16\pi}\int_0^\infty \mathrm{d}x\,[\alpha_\parallel(\mathrm{i}x) + 3\alpha_\perp(\mathrm{i}x)]\,\frac{\omega_\mathrm{s}^2}{x^2 + \omega_\mathrm{s}^2} \tag{12a}$$

and for $H_2$ perpendicular to the surface.

$$C^\parallel = \frac{1}{16\pi}\int_0^\infty \mathrm{d}x\,[2\alpha_\parallel(\mathrm{i}x) + 2\alpha_\perp(\mathrm{i}x)]\,\frac{\omega_\mathrm{s}^2}{x^2 + \omega_\mathrm{s}^2} . \tag{12b}$$

For $r_\mathrm{s} = 2$, $\omega_\mathrm{p} = 0.61$ au, $\omega_\mathrm{s} = 0.44$ au, giving $C^\parallel$ = 0.17 au, using eqs. (10) and $C^\parallel$ = 0.16 au using eqs. (11), and $C^\perp$ = 0.18 au using eqs. (10) and $C_\perp$ = 0.17 au using eqs. (11). For the molecule parallel to the surface, $C^\parallel$ should be equal to $2\beta$ [see eq. (2)]. The agreement between the calculated $C^\parallel$ and the fit of the independent effective atoms approach to the Gordon–Kim calculation is good, since $2\beta$ = 0.14 au.

## 4. Molecular potential curves

Using the results of the Gordon–Kim procedure, which lead to values of $U(R,d) - U(R,\infty)$, we add the values of $U(R,\infty) - U(\infty,\infty)$, the molecular potential curve in the absence of the metal. This gives us values of $U(R,d) - U(\infty,\infty)$, i.e. the energy of the

Table 3
Molecular potential curves $[U(R,d) - U(\infty,\infty)]$ (in $cm^{-1}$)

| $R$ (Å) | $d$ = 1.5 Å | $d$ = 2.0 Å | $d$ = 2.5 Å | $d$ = 5 Å |
|---|---|---|---|---|
| parallel configuration | | | | |
| 0.42 | −4133 | −4543 | −4565 | −4405 |
| 0.53 | −27127 | −27533 | −27526 | −27338 |
| 0.63 | −36062 | −36452 | −36426 | −36204 |
| 0.74 | −38232 | −38601 | −38553 | −38300 |
| 0.85 | −37016 | −37365 | −37295 | −37008 |
| 1.06 | −30476 | −30786 | −36678 | −30327 |
| 1.59 | −13032 | −13256 | −13063 | −12585 |
| perpendicular configuration | | | | |
| 0.42 | 24581 | −4499 | −4543 | −4405 |
| 0.53 | 3380 | −27456 | −27500 | −27338 |
| 0.63 | −3929 | −36341 | −36402 | −36204 |
| 0.74 | −4931 | −38452 | −38526 | −38300 |
| 0.85 | −2542 | −37168 | −37264 | −37010 |
| 1.06 | 6119 | −30474 | −30634 | −30329 |
| 1.59 | 26280 | −12646 | −12980 | −12596 |

molecule at internuclear separation $R$, a distance $d$ from the surface relative to the atoms infinitely far from the surface, and each other. These results are given in table 3 for various values of $R$ and $d$. The results indicate that the effect of the surface is to make the *molecular* repulsive wall slightly more repulsive and the attractive part slightly softer for both the parallel and perpendicular orientations.

We believe that the energies found by the GK method for large $R$ and small $d$ are not trustworthy, since as $R$ gets larger, $H_2$ becomes more like two H atoms and the GK method does not give accurate values of open shell systems. However, for small $R$ (i.e. near the molecular equilibrium position), we believe the results are semi-quantitative. We may then calculate the new equilibrium separation of $H_2$ near the metal by fitting $U(R,d) - U(\infty,\infty)$, $d$ fixed, near $R_0$ = 1.4 au to a parabola whose minimum is displaced from $R_0$. These rather small values of $\Delta R_{eq}(d) = R_{eq}(d) - R_0$ are given in table 4. We see that in the parallel configuration, the bond length increases for all $d$ examined, while in the perpendicular configuration, the bond length gets smaller for small $d$ and larger for large $d$. This is consistent with a recent calculation of Nørskov et al. [21], and indicates that as the molecule in the perpendicular configuration is pushed into the metal, the bond tends to contract.

Table 4
Approximate changes in the equilibrium molecular bond distance (in au) as a function of $d$

| $d$ (Å) | $\Delta R_{eq}$ (parallel) | $\Delta R_{eq}$ (perpendicular) |
|---|---|---|
| 1.5 | +0.005 | −0.06 |
| 2.0 | +0.003 | +0.001 |
| 2.5 | +0.002 | +0.002 |

## 5. Conclusions and summary

In the present work, a Gordon–Kim calculation of the adsorption potential curves for $H_2$ near an $r_s = 2$ jellium surface was done and analyzed. In this way, it has been possible to study the regime of small interatomic distances, close to the equilibrium bond distance, as well as close proximity to the surface, which is outside the range of validity of previous approaches to this problem [4–7]. The adsorption curves themselves have predicted well depths of 200–300 $cm^{-1}$ depending on the orientation of the molecule, which is consistent with the limited experimental data. In addition, an effective atom potential was constructed, using the well region of these curves to fit the parameters, and it was shown that the van der Waals constant was predicted surprisingly well by this method, even though the GK method itself cannot predict this. Preliminary calculations of potential energy surfaces for $H_2$–jellium for larger $r_s$ values indicate that the adsorption well is not very sensitive to $r_s$ value near $r_s = 2$. A more detailed discussion of this will be published in a later paper. Finally, the *molecular* potential curves near the minimum ($R$ = 1.4 au) were calculated and it appears that, although these curves are only slightly changed by adsorption, the molecular bond length increases for the parallel configuration for small $d$, and decreases for the perpendicular configuration for small $d$.

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