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Van Der Waals Interaction Between a Molecule and a Solid Surface

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A general expression for the Van der Waals interaction energy between a molecule and a solid surface is derived, which depends on the orientation of the molecule with respect to the surface, and which is valid for all molecule-surface separation z, provided that the retardation effect can be neglected. Two special cases are discussed: (1) molecules with axial symmetry, and (2) molecules with a permanent electric dipole moment. In all cases the leading term of the asymptotic expansion of the energy is the z^{-3} term, same as the atom-surface interaction case. The Van der Waals energy favors the head on position of molecular adsorption on a solid surface with either the axis of symmetry or the direction of the permanent dipole moment perpendicular to the surface. The water molecule H_2O is taken as an example to calculate the permanent dipole moment contribution to the Van der Waals energy, which shows that it has about the same order of magnitude of the contribution from the induced dipole moment for z to be around a few Angstroms.

I. INTRODUCTION

The study of the Van der Waals interaction between an atom (or a molecule) and a solid surface is an important subject in surface science, especially in the problem of physisorption and atom/molecule-surface scatterings. Previous studies of the Van der Waals interaction [1-5] have been mainly on the atom-surface case, and the molecule-surface case has been largely ignored. The main reason for this may be due to the fact that on the average the molecule-surface interaction will be independent of the orientation of each individual molecule and therefore it will be almost the same as the atom-surface interaction. However we think it is worthwhile to give a more detailed study of the molecule-surface Van der Waals interaction because of the following reasons. Firstly, physisorption of an atom or a molecule on a solid surface is the first step for other kinetic processes on the surface, such as chemisorption, catalysis, and oxidation etc.. For the physisorbed molecule case the binding energy is sensitively dependent on molecular orientation with respect to the surface.

This binding energy is mainly due to the Van der Waals attractive interaction between the molecule and the surface, and therefore a detailed knowledge of the orientational dependence of the Van der Waals potential will be useful. Secondly, there are molecules, such as H_2O, which possess permanent electric dipole moments. We expect the Van der Waals interaction between this kind of molecule and a surface will be different from that between a surface and a molecule with no permanent dipole moment. This permanent dipole moment effect is usually not considered in the atom-surface Van der Waals interaction because atoms usually do not possess permanent dipole moments.

Harris and Feibelman [6] did have a paper on the subject of the Van der Waals interaction between a molecule and a surface. Their thoery is based on the asymptotic form of the Van der Waals potential between an atom and a surface

$$U_{\mathrm{VdW}} = -\frac{C}{z^3} + O(z^{-5}), \tag{1}$$

where z is the atom-surface separation and the constant C can be obtained from the Lifshitz's work on Van der Waals forces between two bodies [7],

$$C = \frac{\hbar}{4\pi}\int_0^\infty d\omega\alpha(i\omega)\frac{\epsilon(i\omega)-1}{\epsilon(i\omega)+1}. \tag{2}$$

Here $\alpha(i\omega)$ and $\epsilon(i\omega)$ are, respectively, the analytic continuations onto the imaginary axis of the frequency-dependent scalar atomic polarizability and the dielectric function of the solid. In the atomic case the constant C in Eq.(2) does not have any angular dependence because of the spherical symmetry of an atom, therefore it can not be applied to the case of molecule-surface interaction. Harris and Feibelman [6] extended Eq.(2) to the case of a. molecule having axial symmetry? and obtained an orientational dependence of the constant C. However we think it is worthwhile to give another derivation of the Van der Waals interaction between a molecule and a surface because of the following reasons:

(a) The asymptotic form of Eq.(1) is valid only for large molecule-surface separation z. The length scale to compare is the size of a molecule which is of the order of an Angstrom. The relevant distances for physisorption and molecule-surface scattering are also of the order of an Angstrom. Therefore Eq.(1) is only a very crude approximation to study these phenomena.

(b) Beside the drawback discussed in [a) in the above, Harris and Feibelman's result is valid only for molecules with axial symmetry such as diatomic molecules H_2, O_2, and N_2 etc.. Their result can not be applied to polyatomic molecules, especially for molecules which have permanent electric dipole moments such as water molecule H_2O.

(c) The constant C in Eq.(2) and its extension to the molecule-surface case involve the dielectric function of the surface for all frequencies which are usually not easy to obtain both experimentally and theoretically. In this paper we derive a formula which involves the imaginary part of the wavevector- and frequency-dependent surface density response function which is in principle can be measured experimentally [4] and easy to estimate theoretically [4, 8].

The purpose of this paper is therefore to derive a formula for the Van der Waals potential between a molecule and a solid surface for all molecule-surface separation as long as the retardation effect [9] can be neglected [10]. The most elegant way to do this is by using the second order perturbation approach to calculate the mutual interaction energy between the molecule and the surface, which is originally formulated by Annett and Echenique [11] to study the atom-surface scattering. This is done in Sec. II. In Sec. III we discuss the interaction energy for the two important classes of molecules mentioned above, i.e., molecules with axial symmetry and molecules with a permanent electric dipole moment.

II. THEORY

In this Section we use the second order perturbation approach to derive the molecule-surface Van der Waals potential energy. We proceed along the line as that of the atom-surface Van der Waals potential [11, 12], except that the geometry of a molecule is more complicated than that of an atom and extra work has to be done. Therefore in this Section we only outline the main steps of the theory, and concentrate on how the geometry of the molecule will affect the final result.

We consider a system consisting of a solid surface which occupies the half-space $z < 0$, and a molecule located somewhere outside the surface $z > 0$, in which z is the coordinate perpendicular to the surface. We calculate the Van der Waals energy via a perturbative approach. The unperturbed system consists of the isolated surface and a free molecule which are assumed to be in their respective ground states except that the molecule may have a translational motion with a constant velocity parallel to the surface. The perturbation is due to the Coulomb coupling V between the surface and the molecule

$$V = \int\int d^3r d^3r' \frac{\rho_m(\mathbf{r})\rho_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{3}$$

where $\rho_m(\mathbf{r})$ and $\rho_s(\mathbf{r}')$ are respectively the charge-density operators for the molecule and the surface. The molecular charge-density operator (in atomic units) is

$$\rho_m(\mathbf{r}) = \sum_j Q_j \delta(\mathbf{r} - \mathbf{R}_j) - \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i), \tag{4}$$

where Q_j and $\mathbf{R}_j$ are respectively the charge and the position vector of the jth nucleus, and $\mathbf{r}_i$ is the position vector of the ith electron. N is the total number of electrons, and

$N = \sum Q_j$ for a neutral molecule. Atomic units are used throughout this paper unless otherwise stated.

The first-order perturbation is zero because the surface is everywhere neutral in its ground state. The Van der Waals interaction energy $U_{\rm VdW}$ is therefore due to the second-order perturbation

$$U_{\rm VdW} = \sum_{n,n'} \frac{|<00'|V|nn'>|^2}{\epsilon_0 + E_{0'} - \epsilon_n - E_{n'}}, \tag{5}$$

where $|nn'>$ denotes a state with the molecule in its nth (unperturbed) excited state (with energy ϵ_n) and the surface in its $n'th$ (unperturbed) excited state (with energy $E_{n'}$), and $|00'>$ is the unperturbed initial ground state of the combined molecule-surface system. By an appropriate expansion [12] of the factor $1/|\mathbf{r}-\mathbf{r}'|$in Eq.(3) and by using the property of translational invariance parallel to the surface, Eq.(5) can be rewritten as

$$U_{\rm VdW} = -\sum_n \int_0^\infty \frac{d\omega}{\pi} \int \frac{d^2q}{(2\pi)^2} \frac{2\pi}{q} \frac{|<0|\rho_{\mathbf{q}}|n>|^2}{\epsilon_n - \epsilon_0 + \omega} Im[(D(\mathbf{q},\omega)], \tag{6}$$

where $\mathbf{q}$ is the two-dimensional wavevector parallel to the surface. and, with $\mathbf{r} = (\mathbf{r}_{||}, z)$,

$$\rho_{\mathbf{q}} = \int d^2 r_{||} \int_0^\infty dz \exp(-qz + i\mathbf{q} \cdot \mathbf{r}_{||}) \rho_m(\mathbf{r}), \tag{7}$$

is the Fourier transform, appropriate for systems having a planar surface, of the molecular charge density operator p,(r). The wavevector- and frequency-dependent imaginary part of the surface density response function $Im[D(\mathbf{q}$, w)] is defined as [II]

$$Im[D(\mathbf{q},\omega)] = \frac{2\pi}{q} \int d^2 r_{||} \int_{-\infty}^0 dz \int_{-\infty}^0 dz' \exp(qz + qz' - i\mathbf{q} \cdot \mathbf{r}_{||}) Im[\chi(\mathbf{r}_{||}, z, z', \omega)], \tag{8}$$

where

$$Im[\chi(\mathbf{r}_{||} - \mathbf{r}'_{||}, z, z', \omega)] = \sum_{n'} <0'|\rho_s(\mathbf{r})|n'><n'|\rho_s(\mathbf{r}')|0'> \pi\delta(E_{n'} - E_{0'} - \omega) \tag{9}$$

is the imaginary part of the position-dependent surface density response function. As pointed out in the Introduction, the imaginary part of the surface density response function appears in our formulation instead of the surface dielectric function in the Lifshitz's formula. This has the advantage that it is related to the zeros of the surface dielectric function [S] and can easily be estimated if the sum rule of the surface dielectric function is used [4].

Now the problem is to calculate the matrix element $<0|\rho_{\mathbf{q}}|n>$, where $\rho_{\mathbf{q}}$ is defined in Eq.(7). We consider the molecule to have a translational motion parallel to the surface with velocity $\mathbf{v}_{||}(\mathbf{v}_\perp = 0)$, and proceed to calculate the matrix element $<0|\rho_{\mathbf{q}}|0>$ as in Ref. 12 to obtain

$$U_{VdW}(Z) = -\sum_n \int_0^\infty \frac{d\omega}{\pi} \int \frac{d^2q}{2\pi q} \frac{Im[D(\mathbf{q},\omega)]}{\omega + \omega_{n0} - \mathbf{q}\cdot\mathbf{v}_{\|} + q^2/2M} \times e^{-2qZ} |i(q_x x'_{n0} + q_y y'_{n0}) - q z'_{n0}|^2 . \quad (10)$$

Here Z is the distance between the surface and the center of mass of the molecule; M being the mass of the molecule; $\omega_{n0} = (\epsilon_n - \epsilon_0)$; and $\mathbf{q} = (q_x, q_y)$. The matrix element x'_{n0} is defined, with $\mathbf{r'}_i = (x'_i, y'_i, z'_i)$, as

$$x'_{n0} = \sum_{i=1}^{N} \int \prod_{j=1}^{N} d^3r'_j \psi_n^*(\mathbf{r'}_1, \mathbf{r'}_2, \cdots, \mathbf{r'}_N) x'_i \psi_0(\mathbf{r'}_1 \mathbf{r'}_2, \cdots, \mathbf{r'}_N) = x'^*_{0n} , \quad (11)$$

where $\psi_0\,(\psi_n)$ is the ground (nth excited) state of the molecule with the center of mass at rest, the origin of the position vectors of the electrons $\mathbf{r'}_j, j = 1, 2, \cdots, N$, in Eq.(11) is chosen at the center of mass of the molecule, and the z'-axis is chosen perpendicular to the surface. Matrix elements y'_{n0} and z'_{n0} are defined in the same way with x'_i replaced by y'_i and z'_i respectively. These matrix elements are proportional to the oscillator strengths of the dipole transition of the molecule between the ground state and the excited states and are related to the polarizability of the molecule.

Equation (10) is the most general expression for the Van der Waals interaction energy between a molecule and a solid surface. The expression depends on the surface property $Im[D(\mathbf{q},\omega)]$ and the molecular property x'_{n0}, y'_{n0}, and z'_{n0}. There are two points worthwhile mentioning. The first point is that for molecules with spherical symrnetry, such as monatomic gas molecules, $x'_{n0} = y'_{n0} = z'_{n0}$, then Eq.(10) reduces to the known Van der Waals energy between an atom and a surface [4, 11, 12]. The second point is that the summation over n in Eq.(10) includes the term n = 0, (and implicitly $n' \neq 0$), because the initial unperturbed state is $n = 0$, $n' = 0$. For most molecules $x'_{00} = y'_{00} = z'_{00} = 0$, therefore the n = 0 term has no contribution as in the atom-surface interaction case. However if a molecule has a permanent electric dipole moment, such as water molecule H_2O, then at least one of the three matrix elements x'_{00}, y'_{00}, or z'_{00}, is not zero. In this case the contribution from the $n = 0$ term may be significant because the denominator becomes smaller as ω_{00} = 0. We will discuss this case in the next Section.

III. DISCUSSIONS

In this Section we discuss two important classes of molecules. The first one is molecules with axial symmetry, such as diatomic molecules H_2, O_2, and N_2, etc.. The second one is molecules with a permanent electric dipole moment, such as H_2O molecule.

1. For molecules with axial symmetry we choose the axis of symmetry to lie in the x-_-plane and making an angle θ with the z-axis. By taking into account the symmetry property of the molecule, Eq.(10) becomes

$$U_{\rm VdW}(Z,\theta) = -\sum_n \int_0^\infty \frac{d\omega}{\pi} \int \frac{d^2q}{2\pi q} \frac{Im[D(\mathbf{q},\omega)]}{\omega + \omega_{n0} - \mathbf{q}\cdot\mathbf{v}_{||} + q^2/2M} e^{-2qZ} F(q,\phi,\theta), \tag{12}$$

where

$$\begin{aligned} F(q,\phi,\theta) &\equiv |i(q_x x_{n0}; + q_y y'_{n0}) - q z'_{n0}|^2 \\ &= q^2(\cos^2\phi + \sin 2\phi\cos\theta + \sin^2\phi\cos^2 8 + \sin^2\theta)|\xi_{n0}|^2 \\ &\quad + q^2(\sin^2\phi\sin^2\theta + \cos^2\theta)|\zeta_{n0}|^2 . \end{aligned} \tag{13}$$

In Eq.(13) ϕ is the angle between $\mathbf{q}$ and the z-axis, and the matrix elements ξ_{n0} and ζ_{n0} are defined exactly the same way as in Eq.(11) except that now $\mathbf{r}'_j = (\xi_j, \eta_j, \zeta_j)$ and ζ-axis is taken along the axis of symmetry of the molecule. We note that now the Van der Waals energy as expressed in Eq.(12) depends both on the molecule-surface separation Z and the angle θ bteween the axis of symmetry of the molecule and the surface. Eq.(12) is the general expression and appears to be a complicated one. For practical purpose, however, Eq.(12) can be simplied as we discuss in the following.

We have seen in the atom-surface case [12] that the translational motion of the atom has negligible effect on the Van der Waals energy for *thermal* atoms. We expect that this will also be the case for the molecule-surface interaction, therefore the last two terms in the denominator of Eq.(12), $\mathbf{q}\cdot\mathbf{v}_{||}$ and $q^2/2M$, can be neglected, if we are only interested in thermal molecules. We also expect that $D(\mathbf{q},\omega) = D(q,\omega)$, i.e., the surface density response function will be independent of the direction of $\mathbf{q}$ if the surface is isotropic. Therefore Eq.(12) becomes

$$U_{\rm VdW}(Z,\theta) = -\sum_n A_n(Z)\Big[\frac{1}{6}(f^L_{n0} - f^T_{n0})P_2(\cos\theta) + \frac{1}{3}(f^L_{n0} + 2f^T_{n0})\Big], \tag{14}$$

with the coefficients $A,(Z)$ defined as

$$A,(Z) \equiv \frac{1}{\omega_{n0}} \int_0^\infty \frac{d\omega}{\pi} \int \frac{q^2dq}{2\pi} \frac{Im[D(q,\omega)]}{\omega + \omega_{n0}} e^{-2qZ} . \tag{15}$$

In Eq.(14) $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$ is the Legendre polynomial of order 2, and f^L_{n0} and f^T_{n0} are the dipole oscillator strengths for a transition from the molecular state 0 to state n. The dipole oscillator strengths are defined (in the conventional units) as

$$f^L_{n0} = \frac{2m\omega_{n0}}{\hbar}|\zeta_{n0}|^2 , \tag{16}$$

and

$$f^T_{n0} = \frac{2m\omega_{n0}}{\hbar}|\xi_{n0}|^2 . \tag{17}$$

where m is the electron mass, and the superscripts L and T denote longitudinal and transverse, respectively, to the axis of symmetry of the molecule. For the purpose of reference we recall that the oscillator strength and the molecular polarizability $\alpha(\omega)$ are related to each other by the following relation:

$$\alpha^s(\omega) = \sum_n \frac{f^s_{n0}}{\omega^2_{n0} - \omega^2}, \qquad s = L, T. \tag{18}$$

Equations (14) and (15) are the expressions for the Van der Waals interaction energy between a molecule with axial symmetry and a solid surface. We make the following remarks:

(a) Equation (15) is not in a form of inverse power series espansion of the molecule surface separation Z, and it is valid for all Z provided that the retardation effect [9] and the translational motion [13] of the molecule can be neglected. If we expand $Im[D(q,\omega)]$ in powers of q, then Eq.(15) will give the coefficients $A,(Z)$ as inverse power series expansion of Z. Substituting these into Eq.(14) one obtains $U_{\rm VdW}$ as inverse power series expansion of Z. The leading term gives the Z^{-3}-law which comes from the q^0 term of the expansion [4] of $Im[D(q,\omega)]$. This is exactly the same as the atomic case, except that in the molecular case the interaction also depends on the angle θ, the orientation of the axis of symmetry of the molecule.

(b) From the definitions Eqs.(16) and (17), we see that both f^L_{n0} and f^T_{n0} are positive quantites, and for molecules with axial symmetry we have, in general, $f^L_{n0} > f^T_{n0}$. Therefore the maximun Van der Waals attractive interaction energy occurs at the angle $\theta = 0$, because $A,(Z)$ are also positive by Eq.(15). This means that a physisorbed molecule favors a head on position, i.e., with the axis of symmetry of the molecule perpendicular to the surface. This is consistent with Harris and Feibelman's result [6]. If we assume that $f^L_{n0} = \gamma f^T_{n0}$ for all n, with $\gamma > 1$ and independent of n, then the ratio of the Van der Waals attractive energy at the same Z for the head on position ($\theta = 0$) and the flat position ($\theta = 90°$) is given by

$$\frac{U_{\rm VdW}(Z,\theta = 0)}{U_{\rm VdW}(Z,\theta = 90°)} = \frac{2(\gamma + 1)}{\gamma + 3}. \tag{19}$$

For H_2 molecules $\gamma \sim 1.33$, therefore the adsorption energy ratio between the head on and the flat positions is about 1.08. This means that the head on position is favored because the magnitude of the attractive energy is larger by about 8% in comparison with that of the flat position adsorption.

(c) For the problem of physisorption one still has to consider the Pauli repulsive energy, because the binding energy for physisorption is the sum of the Van der Waals attractive energy and the Pauli repulsive energy. For Z in the order of 3 or 4 Å, a molecule adsorbed in a flat position usually has a lower repulsive energy than that of a molecule adsorbed in the head on position, i.e., the Pauli repulsive energy favors the flat position adsorption. Therefore there is a competition between the Van der Waals attractive energy and the Pauli repulsive energy, and this may alter the result given in (b). Because it is usually not easy to calculate the Pauli repulsive energy, we therefore will not discuss this subject any further. This subject may be settled by experiment.

2. For molecules with a permanent dipole moment, we have to consider the direction of the dipole moment with respect to the surface. Suppose that the permanent dipole moment **p** lies in the xz-plane and makes an angle θ with the z-axis. Then we have $x'_{00} = p\sin\theta$, $y'_{00} = 0$, and $z'_{00} = p\cos\theta$, and Eq.(10) becomes

$$\begin{aligned} &U_{\rm VdW}(Z,\theta) \\ &= -p^2\int_0^\infty \frac{d\omega}{\pi}\int\frac{d^2q}{2\pi q}\frac{Im[D(\mathbf{q},\omega)]}{\omega-\mathbf{q}\cdot\mathbf{v}_{||}+q^2/2M}e^{-2qZ}(q_x^2\sin^2\theta+q^2\cos^2\theta) \\ &-\sum_{n\neq 0}\int_0^\infty\frac{d\omega}{\pi}\int\frac{d^2q}{2\pi q}\frac{Im[D(\mathbf{q},\omega)]}{w+\omega_{n0}-\mathbf{q}\cdot\mathbf{v}_{||}+q^2/2M} \\ &\times e^{-2qZ}|i(q_xx'_{n0}+q_yy'_{n0})-qz'_{n0}|^2 . \end{aligned} \tag{20}$$

The first term in Eq.(20) is the energy due to the permanent dipole moment and the second term is due to the induced dipole moment, i.e., the polarization effect. Because here we are interested in the effect of the permanent dipole moment only, we discuss the first term in the following. We make the same approximation in deriving Eq.(14), and obtain

$$U^0_{\rm VdW}(Z,\theta) = -\frac{1}{3}p^2[P_2(\cos\theta)+2]\int_0^\infty\frac{d\omega}{\pi}\int\frac{dq}{2\pi}\frac{Im[D(q,\omega)]}{\omega}q^2e^{-2qZ}\,, \tag{21}$$

where the superscript 0 denotes the contribution from the ***permanent*** dipole moment only. We see that Eq.(21) also favors the *head* on (6 = 0) adsorption of the molecule with the direction of the permanent electric dipole moment p perpendicular to the surface. We also note that the leading term of the asymptotic expansion of $U^0_{\rm VdW}(Z)$ is the Z^{-3} term, same as the Van der Waals energy due to the induced dipole moment.

Finally we give H_2O molecule as an example to estimate the magnitude of $U_{\rm VdW}(Z)$ for Z around $3\mathring{A}$, the usual physisorption separations. For [14] H_2O, p = 1.9 x 10^{-18} esu-cm, and using the surface-plasrnon-pole approximation [4] for $Im[D(q,\omega)]$, we obtain $|U^0_{\rm VdW}(Z,\theta)| \sim$ 10 meV for $Z\sim 3\mathring{A}$ and θ = 0. This is about the same order of magnitude of the Van der Waals energy due to the induced dipole moment at the same Z. Therefore both the permanent and the induced dipole moments are equally important in the calculation of the Van der Waals energy between a molecule and a solid surface.

In conclusion we have derived a general formula for the Van der Waals energy between a molecule and a solid surface. which depends on the orientation of the molecule. 111 particular we discussed the cases of molecules with axial symmetry and molecules with a permanent dipole moment. We find that for all cases the leading term of the asymptotic expansions of the energy is the Z^{-3} term as in the atom-surface case. In gereral the Van der Waals energy favors the head on position for molecular adsorption on the surface, with the axis of symmetry or the direction of the permanent dipole moment perpendicular to the surface.

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