Brief Reports

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Exchange-energy contribution to the interaction of helium with a metal surface

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The interaction of helium with a metal surface can be obtained by calculating both the change of the adatom orbital energies and the energy associated with the orthogonalization process which take place during physisorption. The present approach uses the nonlocal expression in order to describe the contribution of the exchange energy in the He-metal interaction, but it does not employ the perturbation series expansion in the He pseudopotential. It is shown that by imposing the condition of self-consistency, a more repulsive expression for the helium interaction is obtained as compared to that of first-order pseudopotential theory. The condition of self-consistency accounts for the major part of the contribution of the higher than first-order terms of the perturbation series in the helium pseudopotential.

In a recent Rapid Communication, Manninen, Nørskov, Puska, and Umrigar[1] discussed the Esbjerg and Nørskov (EN) equation[2] in connection with the problem of the interaction of helium with a metal surface. In its corrected form, the EN equation states that the repulsive interaction $E_{\mathrm{EN}}(\mathbf{r})$ between the He atom and a metal surface is proportional to the (unperturbed) electron density of the substrate $\rho(\mathbf{r})$, i.e.,

$$E_{\mathrm{EN}}(\mathbf{r})=\alpha_{\mathrm{eff}}\rho(\mathbf{r}) \quad , \tag{1}$$

where the proportionality constant α_{eff} depends on the substrate.

Values for α_{eff} obtained with various calculational methods are quite different.[2–6] Of particular interest are the values of α_{eff} obtained within the local-density approximation (LDA) method[2–4] (to the exchange and correlation effects of the He-substrate system) and the values obtained by a method which takes into account the nonlocality of the exchange effects but ignores correlation effects in the He-metal interaction. The values of α_{eff} obtained within the nonlocal scheme are much greater than those obtained within the LDA method. It was then argued[1] that this discrepancy may be due either to the neglect of the correlation effects in the nonlocal approach, or to the problem of convergence associated with the perturbation series expansion in the He pseudopotential which is present in the nonlocal approach.[5,6]

In this Brief Report, we show that one of the two reasons the mentioned discrepancy is associated with may be eliminated. In particular, it is shown that the perturbation series expansion may be replaced by a new expression which, in addition, satisfies the condition of self-consistency. Our proof is based on the assumption (of the pseudopotential approach) that the presence of the He atom in the substrate region has the effect of forcing the single-electron wave functions of the substrate to become orthogonal to the adatom (He) orbitals. Thus, it is assumed that the single-electron wave functions $|\mathbf{k}\rangle$ of the substrate in the presence of the adatom are given with respect to a pseudo wave function $|\mathbf{k}_{\mathrm{ps}}\rangle \simeq |\mathbf{k}_0\rangle$, where $|\mathbf{k}_0\rangle$ are the single-electron wave functions of the free substrate, i.e.,

$$|\mathbf{k}\rangle = |\mathbf{k}_0\rangle - \tilde{\sum_{\alpha}} \langle\alpha|\mathbf{k}_0\rangle\,|\alpha\rangle \quad , \tag{2}$$

where the tilde indicates that the summation does not include spin, $|\alpha\rangle$ denotes the adatom orbitals, and the sum is over these orbitals. The coefficient $\langle\alpha|\mathbf{k}_0\rangle$ is the overlap $S_{\alpha\mathbf{k}}$. It is apparent that $\langle\alpha|\mathbf{k}\rangle=0$ as both the basis sets $\{|\mathbf{k}_0\rangle\}$ and $\{|\alpha\rangle\}$ are assumed to be orthonormal. Our procedure is not based on building up a pseudopotential. Instead, we proceed as follows.

Let V_1 be the perturbation, introduced in the Hamiltonian of the free substrate H_0, and assume

$$H|\mathbf{k}\rangle = (H_0+V_1)|\mathbf{k}\rangle = \epsilon_{\mathbf{k}}|\mathbf{k}\rangle \quad , \tag{3}$$

$$H_0|\mathbf{k}_0\rangle = \epsilon_{\mathbf{k}}^{(0)}|\mathbf{k}_0\rangle \quad . \tag{4}$$

Similarly, for the free and physisorbed adatom it is assumed that

$$H_\alpha|\alpha_0\rangle = \epsilon_\alpha^{(0)}|\alpha_0\rangle \quad , \tag{5}$$

$$(H_\alpha+V_2)|\alpha\rangle = \epsilon_\alpha|\alpha\rangle \quad , \tag{6}$$

where H_α is the free-adatom Hamiltonian and V_2 its perturbation when the adatom is in the presence of the substrate.

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For completeness we define V_1 and V_2:

$$V_1\Psi_{\mathbf{k}}^{(0)} = V_{\mathrm{Cb}}^{(A)}\Psi_{\mathbf{k}}^{(0)} - \tilde{\sum_{\alpha}}\int \frac{\Psi_{\mathbf{k}}^{(0)}(\mathbf{r}')\Psi_{\alpha}^{*(0)}(\mathbf{r}')\Psi_{\alpha}^{(0)}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' = (V_{\mathrm{Cb}}^{(A)} + V_x^{(1)})\Psi_{\mathbf{k}}^{(0)} \ , \tag{7}$$

$$V_2\Psi_{\alpha}^{(0)} = V_{\mathrm{Cb}}^{(M)}\Psi_{\alpha}^{(0)} - \tilde{\sum_{\mathbf{k}}}\int \frac{\Psi_{\alpha}^{*(0)}(\mathbf{r}')\Psi_{\mathbf{k}}^{(0)}(\mathbf{r}')\Psi_{\mathbf{k}}^{(0)}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' = (V_{\mathrm{Cb}}^{(M)} + V_m^{(2)})\Psi_{\alpha}^{(0)} \ , \tag{8}$$

in terms of the Coulomb potential $V_{\mathrm{Cb}}^{(M)}$ and $V_{\mathrm{Cb}}^{(A)}$ due to the free substrate and the free adatom, respectively, and in terms of $V_x^{(1)}$ and $V_x^{(2)}$, the corresponding exchange interaction terms. The notation $\Psi_{\mathbf{k}}^{(0)}$ and $\Psi_{\alpha}^{(0)}$ is used instead of $|\mathbf{k}_0\rangle$ and $|\alpha_0\rangle$. Finally the upper indices M and A refer to the metal and the atom, respectively. It is noted that

$$\tilde{\sum_{\mathbf{k}}}\langle\mathbf{k}_0|V_x^{(1)}|\mathbf{k}_0\rangle = \tilde{\sum_{\alpha}}\langle\alpha|V_x^{(2)}|\alpha\rangle \tag{9}$$

and that

$$\sum_{\alpha}\langle\alpha|V_{\mathrm{Cb}}^{(M)}|\alpha\rangle = \sum_{\mathbf{k}}\langle\mathbf{k}_0|V_{\mathrm{Cb}}^{(A)}|\mathbf{k}_0\rangle + AV_{\mathrm{Cb}}^{(M)}(z_l) \ , \tag{10}$$

where A denotes the atomic number of the adatom which is assumed located at the position z_l from the surface of the substrate.

Multiplying by $\langle\mathbf{k}_0|$ both sides of Eq. (3) from the left, it is easily proved that Eqs. (2), (3), and (4) lead to

$$\sum_{\mathbf{k}}(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^{(0)})\left(1 - \tilde{\sum_{\alpha}}|S_{\alpha\mathbf{k}}|^2\right) = \sum_{\mathbf{k}}\langle\mathbf{k}_0|V_1|\mathbf{k}_0\rangle - \tilde{\sum_{\alpha,\mathbf{k}}}S_{\alpha\mathbf{k}}\langle\mathbf{k}_0|V_1|\alpha_0\rangle \ . \tag{11}$$

On the one hand, the first term of the right-hand side (RHS) of Eq. (11) is rewritten [using Eqs. (9) and (10)] as

$$\begin{aligned}\sum_{\mathbf{k}}\langle\mathbf{k}_0|V_1|\mathbf{k}_0\rangle &= \sum_{\mathbf{k}}\langle\mathbf{k}_0|V_{\mathrm{Cb}}^{(A)}|\mathbf{k}_0\rangle + \sum_{\mathbf{k}}\langle\mathbf{k}_0|V_x^{((1)}|\mathbf{k}_0\rangle \\ &= \sum_{\alpha}\langle\alpha_0|V_x^{(2)}|\alpha_0\rangle + \sum_{\alpha}\langle\alpha_0|V_{\mathrm{Cb}}^{(M)}|\alpha_0\rangle - AV_{\mathrm{Cb}}^{(M)}(z_l) \qquad (12a)\\ &= \sum_{\alpha}\delta\epsilon_{\alpha} - AV_{\mathrm{Cb}}^{(M)}(z_l) \\ &\cong E^{\mathrm{CHF}}(z_l) - E_{\mathrm{free}}^{\mathrm{HF}} - AV_{\mathrm{Cb}}^{(M)}(z_l) \ , \qquad (12b)\end{aligned}$$

where $\delta\epsilon_{\alpha}$ is the perturbation of the eigenvalues of the free adatom upon physisorption. It is also assumed that the difference of the total Hartree-Fock (HF) energies, $E^{\mathrm{CHF}}(z_l)$ and $E_{\mathrm{free}}^{\mathrm{HF}}$, of the physisorbed adatom (coupled HF) and the free adatom, respectively, may be approximated as a summation over the difference of the orbital eigenvalues. On the other hand, the last term of the RHS of Eq. (11) can be rewritten as (by adding and subtracting H_0 to V_1)

$$\tilde{\sum_{\alpha,\mathbf{k}}}\langle\mathbf{k}_0|V_1|\alpha\rangle S_{\alpha\mathbf{k}} = \tilde{\sum_{\alpha,\mathbf{k}}}[-\epsilon_{\mathbf{k}}^{(0)} + V_{\mathrm{eff}}(z_l) + \epsilon_{\alpha}^{(0)}]|S_{\alpha\mathbf{k}}|^2 \ , \tag{13}$$

where $V_{\mathrm{eff}}(z)$ is the single-electron potential for the substrate.[8] Thus Eq. (11) becomes [omitting the factor $(1-\tilde{\sum}_{\alpha}|S_{\alpha\mathbf{k}}|^2)$]

$$\sum_{\mathbf{k}}(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^{(0)}) = E^{\mathrm{CHF}}(z_l) - E_{\mathrm{free}}^{\mathrm{HF}} - AV_{\mathrm{Cb}}(z_l) + \tilde{\sum_{\alpha,\mathbf{k}}}[\epsilon_{\mathbf{k}}^{(0)} - V_{\mathrm{eff}}(z_l) - \epsilon_{\alpha}]|S_{\alpha\mathbf{k}}|^2 \ . \tag{14}$$

A numerical calculation of the term $1-\tilde{\sum}_{\alpha}|S_{\alpha\mathbf{k}}|^2$ indicates that the omission of this term introduces a maximum error of $\pm 2\%$ in the value of $\sum_{\mathbf{k}}(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^{(0)})$ [at $z_l = 5.0$ a.u. from the Al(100) surface].

Equation (14) is the one obtained by Harris and Liebsch[5] within the first-order perturbation term introduced by the pseudopotential of helium.

The three first terms of the RHS of Eq. (14) represent an energy term, ΔE_1, which is approximately due to the exchange interaction $V_x^{(2)}$ as it is directly verified from Eq. (12a) as the term

$$\sum_{\alpha}\langle\alpha_0|V_{\mathrm{Cb}}^{(M)}|\alpha_0\rangle \cong AV_{\mathrm{Cb}}^{(M)}(z) \ .$$

The fourth term of the RHS of Eq. (14), denoted by ΔE_2, is due to the orthogonalization procedure. Although not explicitly shown, the ΔE_1 term is also proportional to the overlap square $|S_{\alpha\mathbf{k}}|^2 = |\langle\mathbf{k}_0|a_0\rangle|^2$.

Application of Eq. (14) may lead to unphysical results. The term ΔE_1 will appear strongly attractive as this term is proportional to the overlap square $|S_{\alpha\mathbf{k}}|^2$. This is mainly due to the fact that the use of an exchange interaction of the form

$$\langle\mathbf{k}|V_x^{(1)}|\mathbf{k}\rangle = -\tilde{\sum_{\alpha}}\int \frac{\Psi_{\mathbf{k}}(\mathbf{r})\Psi_{\alpha}(\mathbf{r})\Psi_{\alpha}(\mathbf{r}')\Psi_{\mathbf{k}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \tag{15}$$

presupposes the orthonormality of the total set $\{\Psi_{\mathbf{k}}, \Psi_a\}$ of the single-electron wave functions, a condition which is not met in the set $\{\Psi_{\mathbf{k}}^{(0)}, \Psi_a^{(0)}\}$. In order to eliminate this drawback one can use the wave functions $|\mathbf{k}\rangle$, as obtained using Eq. (2) in evaluating the exchange term $\langle\mathbf{k}_0|V_x^{(1)}|\mathbf{k}_0\rangle$. This substitution has approximately the result of doubling the ΔE_2 term.

This observation indicates the importance of self-consistency in evaluating the repulsive interaction $\Delta E = \sum_{\mathbf{k}}(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^{(0)})$ upon physisorption.[7] A more accurate expression can be obtained by multiplying both sides of Eq. (3) (from the left) with the wave function $\langle\mathbf{k}|$ (instead of multiplying by $\langle\mathbf{k}_0|$). Following the same procedure we obtain, for the case of He, a repulsive interaction ΔE,

$$\Delta E' = \sum_{\mathbf{k}}(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^{(0)}) = E^{\mathrm{CHF}}(z_l) - E_{\mathrm{free}}^{\mathrm{HF}} - AV_{\mathrm{Cb}}(z_l) + \sum_{\alpha,\mathbf{k}}|S_{\alpha\mathbf{k}}|^2(-V_{\mathrm{eff}} - \epsilon_{\alpha}) \ , \tag{16}$$

which is more repulsive than the expression given by Eq. (14); it is approximately 10% more repulsive in the case of He/Al(100). This is due to the fact the $\epsilon_{\mathbf{k}}$ term which is present in the last term of the RHS of Eq. (14), does not appear in the corresponding term of Eq. (16).

Equation (16) is consistent with the restrictions in the use of the nonlocal expression [given by Eq. (15)] for the exchange energy contribution to the He-metal interaction. Furthermore, it is noted, that by imposing the condition of self-consistency, we allow changes to the unperturbed states $|\mathbf{k}_0\rangle$ which take place during physisorption. Thus, within the approximation described by Eq. (2), Eq. (16) contains most of the contribution of the higher (than the first) terms of the perturbation series in the helium pseudopotential. This is true, in particular, in the case of simple metal substrates for which the approximation $|\mathbf{k}_{\rm ps}\rangle \simeq |\mathbf{k}_0\rangle$ is well justified. A small error may be assigned to the fact that within the approximation of Eq. (2) the single-electron states $|\mathbf{k}\rangle$ of the perturbed substrate are not any longer orthogonal to each other. This will have the effect of introducing an error in calculating the exchange energy contribution to the total energy of the perturbed substrate.

The repulsive interaction we calculated for the He/Al(100) system according to Eq. (16) and using exact wave functions $|\mathbf{k}_0\rangle$ for the substrate[8] and employing the coupled Hartree-Fock method[9] to evaluate the term $E^{\rm CHF}(z_l)$, results in a proportionality constant $\alpha_{\rm eff} \simeq 860$ eV a_0^3. This constant refers to the regions where the free-electron density $\rho(z)$ of the substrate is very small $[\rho(z) \rightarrow 0]$. At higher free-electron densities this constant gets smaller.[10]

The value of $\alpha_{\rm eff}$ found here is approximately of the same magnitude as that found by Harris and Liebsch.[5] Therefore, the remaining discrepancy between the values of $\alpha_{\rm eff}$ found within the present approach and the one found within the LDA method, cannot be attributed to the problems of convergence of the perturbation series in the helium pseudopotential; it may be attributed to the omission of the correlation effects from the attractive term ΔE_1. Other reasons for this discrepancy are discussed in Ref. 10.

In our case ΔE_1 is less negative as compared with the corresponding term of Harris and Liebsch.[5] This is due to the approximation

$$\sum_{\alpha} \delta\epsilon_{\alpha} \simeq E^{\rm CHF}(z_l) - E^{\rm HF}_{\rm free} \quad . \tag{17}$$

It is also noted that the calculation of $E^{\rm CHF}(z_l)$ is very sensitive to the approximation used in evaluating the exchange integrals.[9] The approximation used in Ref. 9 may overestimate[10] the pole $\boldsymbol{\rho} = \boldsymbol{\rho}'$ in the exchange integrals, in particular, in the case of diffusive Gaussian basis functions. This overestimation makes the RHS of Eq. (17) more negative. However, this is avoided here by using a slightly different approximation which is described in detail elsewhere.[10]

In concluding, it is emphasized in this Brief Report that self-consistency is a very important factor in calculating the energy change $\Delta E = \sum_{\mathbf{k}} (\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^{(0)})$ upon physisorption. This energy change can be obtained as follows.

(i) Calculating the change of the orbital energies of the adatom due to physisorption.

(ii) Calculating the energy change associated with the orthogonalization procedure which takes place during physisorption.

(iii) Directly calculating the difference $(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^{(0)})$ rather than independently calculating the eigenvalues $\epsilon_{\mathbf{k}}$ and/or $\epsilon_{\mathbf{k}}^{(0)}$.

It is understood that the above discussion is based on the assumption that the single-electron wave functions of the substrate undergo a change (during He physisorption) which is described within the zeroth order to the He disturbance (pseudopotential). This assumption, however, is expected to approximate quite well the interaction of the noble gases with metal surfaces which are described within the jellium approximation.

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