Physical approach to the $H_2 \leftrightarrow H + H$ reaction: Friction coefficient calculation*

Klaus-Peter Bohnen†
Department of Physics, University of California, San Diego, La Jolla, California 92093 and Max Planck Institut fur Feskörperforschung, 7 Stuttgart 80, Germany

Miguel Kiwi‡
Department of Physics, University of California, San Diego, La Jolla, California 92093 and Departamento de Física e Inmetal, Universidad Simón Bolívar, Caracas, Venezuela

Harry Suhl
Department of Physics, University of California, San Diego, La Jolla, California 92093

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A study of the dynamical aspects related to the $H_2 \leftrightarrow H + H$ reaction on a metal surface is presented. Starting from a model Hamiltonian formulation the binding energy between the two adatoms and the friction coefficient η, both for relative and center-of-mass motion, are calculated. η, which is related to the prefactor in the Arrhenius reaction rate equation, shows variation over a wide range of values as a function of separation between the adatoms. At the same time η exhibits a markedly different behavior depending on whether the adatoms are in a magnetic or nonmagnetic configuration. The implications of our results for recent work on catalysis are briefly discussed.

I. INTRODUCTION

Heterogeneous catalysis has been for a long time a subject of interest for scientists and engineers alike. In particular, the problem of a physical approach to catalysis has recently received renewed attention, both from the theoretical[1-3] and experimental[4-9] point of view. As a result, a growing body of evidence that catalytic rates show significant variations, whenever fluctuations in the substrate degrees of freedom are large, has emerged. These fluctuations may be related to phase transitions, alloying or other causes.

Motivated by this body of evidence Suhl *et al.*[2] have developed a Brownian motion model of the interactions between chemical species and metallic electrons; the resulting formalism provides a general expression for the friction coefficient η of the reactants over the surface of the catalyst. This coefficient η, in turn, determines the value of the prefactor ν in the Arrhenius reaction rate equation

$$\kappa = \nu \exp(-F_B/k_B T) , \tag{1.1}$$

where κ is the reaction rate, T the temperature, k_B the Boltzmann constant, F_B the barrier free energy, and the prefactor ν is an "attempt" frequency to overcome the barrier.

Kramers[10] assumed that the time evolution equation for the distribution function for one-dimensional motion of the adatoms along the reaction path has Fokker-Planck form; the validity and limitations of using this equation within the context of a quantum-mechanical formulation of the problem, have recently been discussed by Schaich.[3] While a general solution for the Fokker-Planck equation has not been obtained yet, Kramers[10] was able to obtain approximate solutions in the small- and large-η limits; these solutions have the form of Eq. (1.1) with

$$\nu \propto \eta/k_B T \quad \text{for } \eta < \omega_A k_B T/V_B$$

and

$$\nu \propto \omega_A \omega_B/\eta \quad \text{for } \eta > \omega_B ,$$

where

$$\omega_{A,B} = \frac{2}{M} \left| \frac{\partial^2 V}{\partial R^2} \right|_{A,B} \tag{1.2}$$

are related to the curvature at the top and bottom of the potential barrier $V(R)$, while M is the mass of the reactant atoms. On the other hand, Kramers also presented evidence to show that in the intermediate region (i.e., $\omega_B < \eta < \omega_A k_B T/V_B$) the kinematic theory of Eyring *et al.*,[11] known as absolute rate theory (ART), does apply. In fact, it is widespread practice to assume that ν is simply a constant and that ART always applies.

To explore the validity of such a procedure we have carried out and reported previously[12] a model calculation for the friction coefficient η of an adsorbed H atom on a metal surface, using the formalism proposed in Ref. 2. Our results supported the claim that ART may not always be applicable.

The model we invoked in our previous publication followed the spirit of the treatment given by Newns[13] for the chemisorption of an H atom on a transition-metal surface. In this paper we carry out a natural generalization of the model, in order

to treat the significantly more complex reaction $H_2 \rightarrow H+H$. In Sec. II this model is formalized by writing a Hamiltonian; however, in order to make the problem tractable a truncation of the Hamiltonian proves to be necessary. The effective Hamiltonian thus obtained is treated by means of Green's-function techniques[14]; details of this treatment are provided in Appendix B.

While our model Hamiltonian does include many essential electron correlations, it does not incorporate directional forces from neighboring atoms nor the vibrational motion of surface ions (phonons), and thus several important aspects in the description of catalytic processes are not dealt with in this contribution.

Knowledge of these Green's functions allows the binding energy between two hydrogen atoms in an electron gas to be evaluated; this calculation is carried out in Sec. III. Next, the friction coefficient η is obtained in Sec. IV, while numerical results, both for the binding energy and the friction coefficient as functions of interatomic distance, are computed in Sec. V. A general discussion of the results thus obtained and a summary of the main conclusions that can be drawn, closes the paper. Several subsidiary matters are dealt with in Appendices A–D.

II. HAMILTONIAN FORMULATION

In this section we formalize the model outlined in the Introduction; as mentioned, for the purposes we are interested in it is reasonable to replace the actual system, of two H atoms adsorbed on a metal surface, by the idealized model of two H atoms in an electron gas; in doing so we follow quite closely the spirit of the presentation of Newns[13] for the analogous one-atom case. In assuming this idealized model we lose all effects which are explicitly related to the presence of the surface.

The first step in the formalization is to choose as our basis set the 1s wave functions $|a_1\rangle$ and $|a_2\rangle$ of the two H atoms, plus the electron gas eigenstates $\{|\vec{k}\rangle\}$; moreover, for the time being and in order not to complicate excessively this model calculation, intended principally to clarify and illustrate the main features of the process, we neglect nonorthogonality effects between $\{|\vec{k}\rangle\}$ and $|a_1\rangle, |a_2\rangle$.[15] The latter are orthogonal to each other only at large distances; thus, we choose the mutually orthogonal linear combination

$$|\pm\rangle = [1/(2 \pm 2\Delta)^{1/2}]|a_1\rangle \pm [1/(2 \pm 2\Delta)^{1/2}]|a_2\rangle , \tag{2.1}$$

where $\Delta(R) \equiv \langle a_1 | a_2 \rangle$ is the overlap integral when the nuclei (protons) are a distance R apart. $|+\rangle$ and $|-\rangle$ are the bonding and antibonding wave functions for the molecular hydrogen ion, respectively.

As our model Hamiltonian we write

$$H = \mathcal{H}_m + H_H + \mathcal{H}_{m\text{-}H} , \tag{2.2}$$

where $\mathcal{H}_m$ describes the metal (idealized as an electron gas), H_H represents the H atoms, and $\mathcal{H}_{m\text{-}H}$ is the coupling term between the metal and the hydrogen atoms. Within our basis $\{|\vec{k}\rangle, |a_1\rangle, |a_2\rangle\}$ we have

$$\mathcal{H}_m = \sum_{\vec{k},\sigma} \epsilon_k \hat{n}_{\vec{k}\sigma} , \tag{2.3}$$

$$\begin{aligned} H_H = {} & \sum_{\sigma} (\epsilon_+ \hat{n}_{+,\sigma} + \epsilon_- \hat{n}_{-,\sigma}) + \tilde{U}_{++} \hat{n}_{+,\uparrow} n_{+,\downarrow} + \tilde{U}_{--} \hat{n}_{-,\uparrow} \hat{n}_{-,\downarrow} \\ & + \sum_{\sigma} (\tilde{U}_{+-} \hat{n}_{+,\sigma} \hat{n}_{-,-\sigma} + \tilde{U}'_{+-} \hat{n}_{+,\sigma} \hat{n}_{-,\sigma}) \\ & + U_{++--} (a^\dagger_{+,\uparrow} a^\dagger_{+,\downarrow} a_{-,\downarrow} a_{-,\uparrow} + a^\dagger_{-,\uparrow} a^\dagger_{-,\downarrow} a_{+,\downarrow} a_{+,\uparrow}) \\ & + U_{+-+-} \sum_{\sigma} a^\dagger_{+,\sigma} a^\dagger_{-,-\sigma} a_{+,-\sigma} a_{-,\sigma} + \frac{e^2}{R} , \end{aligned} \tag{2.4}$$

$$\mathcal{H}_{m\text{-}H} = \frac{1}{(N)^{1/2}} \sum_{\vec{k},\sigma} (V_{+,\vec{k}} a^\dagger_{+,\sigma} c_{\vec{k},\sigma} + V_{-,\vec{k}} a^\dagger_{-,\sigma} c_{\vec{k}\sigma} + \text{H.c.}) , \tag{2.5}$$

where

$$\hat{n}_{\vec{k}\sigma} = c^\dagger_{\vec{k},\sigma} c_{\vec{k},\sigma} , \quad \hat{n}_{\pm,\sigma} = a^\dagger_{\pm,\sigma} a_{\pm,\sigma} .$$

The operators $c^\dagger_{\vec{k}\sigma}$ ($c_{\vec{k}\sigma}$) are creation (destruction) operators for metal electron states, while $a^\dagger_{\pm,\sigma}$ ($a_{\pm,\sigma}$) are creation (destruction) operators for electrons in the bonding and antibonding states of the molecular hydrogen ion. The hopping matrix element is given by

$$V_{\pm,\vec{k}} = \int \langle \pm | V | k \rangle d^3 r , \tag{2.6}$$

where V is the bare electron-ion potential plus an effective potential V^{eff} describing the electron-electron interactions in the substrate; electron-electron correlations in the localized levels are incorporated through the bonding and antibonding states $|\pm\rangle$. The matrix elements $U_{++}, \tilde{U}_{--}$, U_{+-}, U_{++--}, and U_{+-+-} are linear combinations of Coulomb and exchange integrals defined in Appendix A, where expressions for the single-particle energies $\epsilon_\pm$ are also to be found.

Unfortunately, our Hamiltonian as formulated in Eqs. (2.2)–(2.5) does give rise to an extremely complicated set of self-consistency equations for the occupation numbers $\langle \hat{n}_{\pm,\sigma} \rangle$ and the expectation values $\langle a^\dagger_{+,\sigma} a_{-,\sigma} \rangle$, $\langle a^\dagger_{+,\sigma} a_{+,-\sigma} \rangle$, and $\langle a^\dagger_{+,\sigma} a_{-,-\sigma} \rangle$, which arise from the terms proportional to U_{++--} and U_{+-+-} in H_H; this set of self-consistency equations does not seem to be tractable analytically even in the Hartree-Fock approximation, and thus we have to invoke an additional approximation.

In the absence of a metal H_H is the Hamiltonian for two hydrogen atoms treated in molecular-orbital theory, including configuration interactions; precisely these configuration interactions give rise to the terms proportional to U_{++--} and U_{+-+-}. Neglect of these terms leads to completely wrong values of the binding energies for large separation between the two hydrogen atoms. We thus retain configuration interactions phenomenologically through the following renormalization:

$$U_{++} = \tilde{U}_{++} - \alpha U_{++--}, \tag{2.7a}$$

$$U_{--} = \tilde{U}_{--} + \alpha U_{+--+}, \tag{2.7b}$$

$$U_{+-} = \tilde{U}_{+-} + \alpha U_{+-+-}, \tag{2.7c}$$

$$U'_{+-} = \tilde{U}'_{+-}, \tag{2.7d}$$

where α is a function of the overlap integral $\Delta \equiv \langle a_1 | a_2 \rangle$ chosen to give a good fit to the energy[16] in molecular-orbital theory. The required fit is obtained with

$$\alpha = 1/(1+\Delta)^2 . \tag{2.8}$$

Thus, the final form of our Hamiltonian is

$$\mathcal{H} = \mathcal{H}_m + \mathcal{H}_H + \mathcal{H}_{m\text{-}H}, \tag{2.9}$$

with $\mathcal{H}_m$ and $\mathcal{H}_{m\text{-}H}$ given in Eqs. (2.3) and (2.5), respectively, and

$$\mathcal{H}_H = \sum_\sigma (\epsilon_+ \hat{n}_{+,\sigma} + \epsilon \hat{n}_{-,\sigma}) = U_{++}\hat{n}_{+,\uparrow}\hat{n}_{+,\downarrow} + U_{--}\hat{n}_{-,\uparrow}\hat{n}_{-,\downarrow} + \sum_\sigma (U_{+-}\hat{n}_{+,\sigma}\hat{n}_{-,-\sigma} + U'_{+-}\hat{n}_{+,\sigma}\hat{n}_{-,\sigma}). \tag{2.10}$$

The binding energy and the friction coefficient which enters in the calculation of the reaction rate, are now evaluated using Green's-function techniques within a Hartree-Fock self-consistency scheme; the details of the Green's-function evaluation can be found in Appendix B. We will use these Green's functions[14] in the calculation of the binding energy which follows.

III. BINDING ENERGY

In this section we evaluate the binding energy between two hydrogen atoms immersed in an electron gas. This binding energy E_B is defined as the difference in energy between the cases when the two atoms are separated by a finite distance R and when they are an infinite distance apart; thus

$$E_B = E(R) - E(\infty), \tag{3.1}$$

and $E(R)$ is given by

$$E(R) = \sum_\sigma \int_{-\infty}^{\epsilon_F} \epsilon \rho_t^\sigma(\epsilon)\, d\epsilon - \sum_\sigma \int_{-\infty}^{\epsilon'_F} \epsilon \sum_{\vec{k}} \rho_{\vec{k}}^\sigma(\epsilon)\, d\epsilon - 2\epsilon_H + \frac{e^2}{R} - U_{++} n_{+,\uparrow} n_{+,\downarrow} - U_{--} n_{-,\uparrow} n_{-,\downarrow} - U_{+-}(n_{+,\uparrow} n_{-,\downarrow} + n_{+,\downarrow} n_{-,\uparrow}) - U'_{+-}(n_{+,\uparrow} n_{-,\uparrow} + n_{+,\downarrow} n_{-,\downarrow}). \tag{3.2}$$

Here ϵ_H is the binding energy of an isolated hydrogen atom and $\rho_t^\sigma(\epsilon)$ is the total density of states per spin direction, related to our Green's functions through

$$\rho_t^\sigma(\epsilon) = -\frac{1}{\pi} \operatorname{Im}\left(\sum_{\vec{k}} G^\sigma_{\vec{k}\vec{k}}(\epsilon) + G^\sigma_{++}(\epsilon) + G^\sigma_{--}(\epsilon) \right). \tag{3.3}$$

The terms with U carry a minus sign since they have been doubly counted in the summation $\sum_\sigma \rho_t^\sigma$.

ϵ_F and ϵ'_F are the Fermi energies of the interacting and noninteracting systems, respectively; since these systems differ by two electrons we have

$$\sum_\sigma \left(\int_{-\infty}^{\epsilon_F} \rho_t^\sigma(\epsilon)\, d\epsilon - \int_{-\infty}^{\epsilon'_F} \sum_{\vec{k}} \rho_{\vec{k}}^\sigma(\epsilon)\, d\epsilon \right) = 2. \tag{3.4}$$

Combination of (3.2) and (3.4) then yields

$$E(R) = \sum_\sigma \int_{-\infty}^{\epsilon_F} (\epsilon - \epsilon_F) \frac{\partial}{\partial \epsilon} \left(-\frac{1}{\pi} \operatorname{Im} \ln[(G^\sigma_{++})^{-1}(G^\sigma_{--})^{-1}] \right) d\epsilon + 2(\epsilon_F - \epsilon_H) + \frac{e^2}{R} - U_{++} n_{+,\uparrow} n_{+,\downarrow} - U_{--} n_{-,\uparrow} n_{-,\downarrow} - U_{+-} \sum_\sigma n_{+,\sigma} n_{-,-\sigma} - U'_{+-} \sum_\sigma n_{+,\sigma} n_{-,\sigma}. \tag{3.5}$$

This result constitutes the natural generalization to the two-adatom case of the expression derived by Newns[13] for the adsorption energy of one adatom. To simplify Eq. (3.5) further, explicit forms for the summations in the expression (B11) for G_{++} and G_{--} are needed; in order to obtain them we note that as a consequence of Eq. (2.6)

$$|V_{\vec{k}\pm}|^2 = [|V_{\vec{k}1}|^2/(1 \pm \Delta)](1 \pm \cos\vec{k}\cdot\vec{R}). \tag{3.6}$$

Thus

$$\frac{1}{N}\sum_{\vec{k}} \frac{|V_{\vec{k}\pm}|^2}{\omega_\pm - \epsilon_k} = \frac{1}{N}\sum_{\vec{k}} \frac{|V_{\vec{k}1}|^2}{\omega_\pm - \epsilon_k} \frac{1 \pm \cos\vec{k}\cdot\vec{R}}{1 \pm \Delta}, \tag{3.7}$$

where $V_{\vec{k}1}$ is the usual Anderson-type[17] matrix element between localized and itinerant one-electron states. The summation is carried out using constant density of states ρ with a band of width $2D$, assuming that $V_{\vec{k}1}$ is independent of the direction of $\vec{k}$ and neglecting the real (principal) part of the integral, to obtain

$$\frac{1}{N}\sum_{\vec{k}} \frac{|V_{\vec{k}\pm}|^2}{\omega_\pm - \epsilon_k} = \mp \frac{i}{1 \pm \Delta} \left(1 \pm \frac{\sin k_F R}{k_F R} \right) \Gamma \equiv \mp i\Omega_\pm, \tag{3.8}$$

where $\Gamma = \pi\rho|V|^2$. Our approximations are reasonable as long as we do not require to know the exact position of split off states below and above the band edges; this limits our results to the weak coupling limit, i.e., to the case when the bandwidth is much larger than the width of the molecular bonding and antibonding states. Substitution of (3.8) in (B11) and combination with Eq. (3.5) yields

$$E(R) = \sum_\sigma \left[\epsilon_{+,\sigma} n_{+,\sigma} + \epsilon_{-,\sigma} n_{-,\sigma} + \frac{1}{2\pi}\left(\Omega_+ \ln \frac{\epsilon_{+,\sigma}^2 + \Omega_+^2}{(D+\epsilon_{+,\sigma})^2 + \Omega_+^2} + \Omega_- \ln \frac{\epsilon_{-,\sigma}^2 + \Omega_-^2}{(D+\epsilon_{-,\sigma})^2 + \Omega_-^2}\right)\right.$$
$$\left. - \frac{D}{\pi}\left(\frac{(D+\epsilon_{+,\sigma})\Omega_+}{(D+\epsilon_{+,\sigma})^2 + \Omega_+^2} + \frac{(D+\epsilon_{-,\sigma})\Omega_-}{(D+\epsilon_{-,\sigma})^2 + \Omega_-^2}\right)\right] - 2\epsilon_H + \frac{e^2}{R}$$
$$- U_{++} n_{+,\uparrow} n_{+,\downarrow} - U'_{--} n_{-,\uparrow} n_{-,\downarrow} - U_{+-} \sum_\sigma n_{+,\sigma} n_{-,-\sigma} - U_{+-} \sum_\sigma n_{+,\sigma} n_{-,\sigma}, \tag{3.9}$$

where $\epsilon_{\pm,\sigma}$ and ϵ_H are measured relative to the Fermi energy and D is the half bandwidth. This concludes the evaluation of the binding energy and everything is now set up for the calculation of the friction coefficient.

IV. FRICTION COEFFICIENT

This section is devoted to the explicit evaluation of the friction coefficient $\eta_{kl}^{\alpha\delta}$; $\alpha, \delta = \{x, y, z\}$ denote the Cartesian components of the kth and lth adparticle displacement vector, respectively. To obtain $\eta_{kl}^{\alpha\delta}$ we use the fluctuation-dissipation expression derived by Suhl *et al.*[2] which reads

$$\eta_{kl}^{\alpha\delta} = \frac{\beta}{M} \operatorname{Re} \int_0^\infty dt \, \langle \hat{\mathfrak{F}}_k^\alpha(0) \hat{\mathfrak{F}}_l^\delta(t) \rangle \, dt, \tag{4.1}$$

where the fluctuating part of the force operator $\hat{F}_k^\alpha$ is given by

$$\hat{\mathfrak{F}}_k^\alpha \equiv \hat{F}_k^\alpha - \langle \hat{F}_k^\alpha \rangle. \tag{4.2}$$

A. Relative motion

Our main concerns are the relative and center-of-mass friction coefficients, that is,

$$\eta_{\mathrm{rel}}^{\alpha\alpha} = \eta_{11}^{\alpha\alpha} - \eta_{12}^{\alpha\alpha} \tag{4.3a}$$

and

$$\eta_{\mathrm{c.m.}}^{\alpha\alpha} = \eta_{11}^{\alpha\alpha} + \eta_{12}^{\alpha\alpha}. \tag{4.3b}$$

Since

$$\langle \hat{\mathfrak{F}}_1(0) \hat{\mathfrak{F}}_1(t) \rangle = \langle \hat{\mathfrak{F}}_2(0) \hat{\mathfrak{F}}_2(t) \rangle, \tag{4.4a}$$

$$\langle \hat{\mathfrak{F}}_1(0) \hat{\mathfrak{F}}_2(t) \rangle = \langle \hat{\mathfrak{F}}_2(0) \hat{\mathfrak{F}}_1(t) \rangle, \tag{4.4b}$$

it follows that

$$\eta_{\mathrm{rel}}^{\alpha\alpha} = \frac{\beta}{2M} \operatorname{Re} \int_0^\infty dt \, \langle [\hat{\mathfrak{F}}_1^\alpha(0) - \hat{\mathfrak{F}}_2^\alpha(0)] [\hat{\mathfrak{F}}_1^\alpha(t) - \hat{\mathfrak{F}}_2^\alpha(t)] \rangle. \tag{4.5}$$

Thus defining

$$\hat{\mathfrak{F}} \equiv \hat{\mathfrak{F}}_1 - \hat{\mathfrak{F}}_2, \tag{4.6}$$

we obtain

$$\eta_{\mathrm{rel}}^{\alpha\alpha} = \frac{\beta}{2M} \operatorname{Re} \int_0^\infty dt \, \langle \hat{\mathfrak{F}}^\alpha(0) \hat{\mathfrak{F}}^\alpha(t) \rangle. \tag{4.7}$$

We write the force operator $\hat{F}^\alpha$ as

$$\hat{F}^\alpha = \hat{I}^\alpha + \hat{J}^\alpha, \tag{4.8}$$

with

$$\hat{I}^\alpha = \sum_s (W_{++}^\alpha \hat{n}_{+,s} + W_{--}^\alpha \hat{n}_{-,s}) \tag{4.9a}$$

and

$$\hat{J}^\alpha = \sum_{\vec{k},s} (W_{\vec{k}+}^\alpha c_{\vec{k}s}^\dagger a_{+,s} + W_{\vec{k}-}^\alpha c_{\vec{k}s}^\dagger a_{-,s} + W_{+,\vec{k}}^\alpha a_{+,s}^\dagger c_{\vec{k}s} + W_{-,\vec{k}}^\alpha a_{-,s}^\dagger c_{\vec{k}s}, \tag{4.9b}$$

where

$$W_{\pm\pm}^\alpha \equiv \frac{1}{2 \pm 2\Delta}\left(2\left\langle a_2 \left| \frac{\partial V(\vec{r}, \vec{R}_1)}{\partial r_\alpha} \right| a_2 \right\rangle - 2\left\langle a_1 \left| \frac{\partial V(\vec{r}, \vec{R}_2)}{\partial r_\alpha} \right| a_1 \right\rangle \right.$$
$$\left. \pm \left\langle a_1 \left| \frac{\partial}{\partial r_\alpha} [V(\vec{r}, \vec{R}_1) - V(\vec{r}, \vec{R}_2)] \right| a_2 \right\rangle \pm \left\langle a_2 \left| \frac{\partial}{\partial r_\alpha} [V(\vec{r}, \vec{R}_1) - V(\vec{r}, \vec{R}_2)] \right| a_1 \right\rangle\right) \tag{4.10}$$

and

$$W_{\vec{k}\pm}^\alpha \equiv \frac{-1}{(2 \pm 2\Delta)^{1/2}}\left(2\left\langle \vec{k} \left| \frac{\partial V(\vec{r}, \vec{R}_2)}{\partial r_\alpha} \right| a_1 \right\rangle \mp 2\left\langle \vec{k} \left| \frac{\partial V(\vec{r}, \vec{R}_1)}{\partial r_\alpha} \right| a_2 \right\rangle + \left\langle \vec{k} \left| \frac{\partial V^{\mathrm{eff}}(\vec{r})}{\partial r_\alpha} \right| a_1 \right\rangle \mp \left\langle \vec{k} \left| \frac{\partial V^{\mathrm{eff}}(\vec{r})}{\partial r_\alpha} \right| a_2 \right\rangle\right). \tag{4.11a}$$

For the following calculations the definitions

$$W^{\alpha}_{\vec{k}1} \equiv -\left\langle k \left| \frac{\partial V^{\rm eff}(\vec{r})}{\partial r_\alpha} \right| a_1 \right\rangle \quad \text{and} \quad W^{\alpha}_{\vec{k}2} \equiv -\left\langle k \left| \frac{\partial V^{\rm eff}(\vec{r})}{\partial r_\alpha} \right| a_2 \right\rangle \tag{4.11b}$$

are useful.

The definition of the force operator (4.11a) excludes terms which do not contribute to the fluctuating force. At the same time, terms related to interactions between electrons in localized levels have been neglected; they do not contribute to the force related to the motion of the center of mass of the two adatoms. We neglect these interactions for the relative motion since their influence would be restricted to very small separations between the adatoms by taking into account screening effects.

Combining Eq. (4.7) with Eq. (4.8) yields

$$\eta^{\alpha\alpha}_{\rm rel} = \frac{\beta}{2M} \mathrm{Re} \int_0^\infty dt [\langle \hat{I}^\alpha(0)\hat{I}^\alpha(t)\rangle + \langle \hat{J}^\alpha(0)\hat{I}^\alpha(t)\rangle + \langle \hat{I}^\alpha(0)\hat{J}^\alpha(t)\rangle + \langle \hat{J}^\alpha(0)\hat{J}^\alpha(t)\rangle]. \tag{4.12}$$

The correlation functions above are evaluated using Green's-function techniques within Hartree-Fock approximation; the details are given in Appendix C. The resulting expressions, valid for $T/T_F \ll 1$ are

$$\eta^{\alpha\alpha}_{\rm rel}(II) = \frac{1}{2\pi M} \sum_\sigma \left((W^\alpha_{++})^2 \frac{\Omega_+^2}{\epsilon^2_{+,\sigma} + \Omega_+^2} + (W^\alpha_{--})^2 \frac{\Omega_-^2}{\epsilon^2_{-,\sigma} + \Omega_-^2} \right), \tag{4.13}$$

$$\eta^{\alpha\alpha}_{\rm rel}(IJ) + \eta^{\alpha\alpha}_{\rm rel}(JI) = -\frac{2}{\pi M} \sum_\sigma \left(W^\alpha_{++} \xi^\alpha_+ \frac{\Omega_+ \epsilon_{+,\sigma}}{(\epsilon^2_{+,\sigma} + \Omega_+^2)^2} + W^\alpha_{--} \xi^\alpha_- \frac{\Omega_- \epsilon_{-,\sigma}}{(\epsilon^2_{-,\sigma} + \Omega_-^2)^2} \right), \tag{4.14}$$

and

$$\eta^{\alpha\alpha}_{\rm rel}(JJ) = \frac{1}{\pi M} \sum_\sigma \left(\gamma^\alpha_+ \frac{\Omega_+}{\epsilon^2_{+,\sigma} + \Omega_+^2} + \gamma^\alpha_- \frac{\Omega_-}{\epsilon^2_{-,\sigma} + \Omega_-^2} - [(\lambda^\alpha_+)^2 + (\lambda^\alpha_-)^2] \frac{\Omega_+}{\epsilon^2_{+,\sigma} + \Omega_+^2} \frac{\Omega_-}{\epsilon^2_{-,\sigma} + \Omega_-^2} \right.$$
$$\left. + 2\lambda^\alpha_+ \lambda^\alpha_- \frac{\epsilon_{+,\sigma}}{\epsilon^2_{+,\sigma} + \Omega_+^2} \frac{\epsilon_{-,\sigma}}{\epsilon^2_{-,\sigma} + \Omega_-^2} - (\xi^\alpha_+)^2 \frac{\Omega_+^2 - \epsilon^2_{+,\sigma}}{\Omega_+^2 + \epsilon^2_{+,\sigma}} - (\xi^\alpha_-)^2 \frac{\Omega_-^2 - \epsilon^2_{-,\sigma}}{\Omega_-^2 + \epsilon^2_{-,\sigma}} \right). \tag{4.15}$$

Here we have used the definitions

$$\Omega_\pm \equiv -\frac{1}{N} \mathrm{Im} \sum_{\vec{k}} \frac{|V_{\vec{k}\pm}|^2}{\omega_+ - \epsilon_+}, \tag{4.16}$$

$$\xi^\alpha_\pm \equiv -\frac{1}{N} \mathrm{Im} \sum_{\vec{k}} \frac{W^\alpha_{\vec{k}\pm} V_{\pm,\vec{k}}}{\omega_+ - \epsilon_k}, \tag{4.17}$$

$$\lambda^\alpha_\pm \equiv -\frac{1}{N} \mathrm{Im} \sum_{\vec{k}} \frac{W^\alpha_{\vec{k}\pm} V_{\pm,\vec{k}}}{\omega_+ - \epsilon_k}, \tag{4.18}$$

$$\gamma^\alpha_\pm \equiv -\frac{1}{N} \mathrm{Im} \sum_{\vec{k}} \frac{|W^\alpha_{\vec{k}\pm}|^2}{\omega_+ - \epsilon_k}, \tag{4.19}$$

with $\omega_+ = \omega + i0^+$.

In obtaining the above results the two main approximations have been made; the first and most important one is the Hartree-Fock approximation, which was used to solve the self-consistent Green's-functions equations (see Appendix B) and to evaluate the correlation functions (see Appendix C). The second major approximation is to treat Ω, ξ, λ, and γ [defined in Eqs. (4.16)–(4.19)] as parameters, while neglecting the real part of their $\vec{k}$ summations, when computing numerically our results.

B. Center-of-mass motion

Having obtained an expression for the friction coefficient for relative motion of two H atoms on a transition metal surface, we now turn our attention to their center-of-mass motion. Owing to the fact that only the sum of the forces on the two atoms is relevant in this case, there is a considerable simplification in the calculation of $\eta^{\alpha\alpha}_{\rm c.m.}$ when compared with the one carried out above for $\eta^{\alpha\alpha}_{\rm rel}$. In fact, combination of Eqs. (4.1), (4.2), and (4.3b) yields

$$\eta^{\alpha\alpha}_{\rm c.m.} = \frac{\beta}{2M} \mathrm{Re} \int_0^\infty dt \langle [\hat{\mathfrak{F}}^\alpha_1(0) + \hat{\mathfrak{F}}^\alpha_2(0)][\hat{\mathfrak{F}}^\alpha_1(t) + \hat{\mathfrak{F}}^\alpha_2(t)] \rangle, \tag{4.20}$$

where $\hat{\mathfrak{F}}^\alpha_k$ is related to the force operator $\hat{F}^\alpha_k$ through Eq. (4.2) and

$$\hat{F}^\alpha_1 + \hat{F}^\alpha_2 = \frac{1}{(N)^{1/2}} \sum_{\vec{k},\sigma} (W^\alpha_{\vec{k}1} c^\dagger_{\vec{k}\sigma} a_{1,\sigma} + W^\alpha_{1,\vec{k}} a^\dagger_{1,\sigma} c_{\vec{k}\sigma}$$
$$+ W^\alpha_{\vec{k}2} c^\dagger_{\vec{k}\sigma} a_{2,\sigma} + W^\alpha_{2,\vec{k}} a^\dagger_{2,\sigma} c_{\vec{k}\sigma}), \tag{4.21}$$

where $W^\alpha_{\vec{k}1}, W^\alpha_{\vec{k}2}$ are given by Eq. (4.11b).

This equation can be rewritten

$$\hat{F}^\alpha_1 + \hat{F}^\alpha_2 = \frac{1}{(2N)^{1/2}} \sum_{\vec{k},\sigma} \left(\frac{W^\alpha_{\vec{k}1} + W^\alpha_{\vec{k}2}}{(1+\Delta)^{1/2}} c^\dagger_{\vec{k}\sigma} a_{+,\sigma} + \frac{W^\alpha_{\vec{k}1} - W^\alpha_{\vec{k}2}}{(1-\Delta)^{1/2}} c^\dagger_{\vec{k}\sigma} a_{-,\sigma} + \frac{W^\alpha_{1,\vec{k}} + W^\alpha_{2,\vec{k}}}{(1+\Delta)^{1/2}} a^\dagger_{+,\sigma} c_{\vec{k}\sigma} + \frac{W^\alpha_{1,\vec{k}} + W^\alpha_{2,\vec{k}}}{(1-\Delta)^{1/2}} a^\dagger_{-,\sigma} c_{\vec{k}\sigma} \right) \tag{4.22}$$

or more simply as

$$\hat{F}_1^\alpha + \hat{F}_2^\alpha = \frac{1}{(2N)^{1/2}} \sum_{\vec{k},\sigma} (w_{\vec{k}+}^\alpha c_{\vec{k}\sigma}^\alpha a_{+,\sigma} + w_{\vec{k}-}^\alpha c_{\vec{k}\sigma}^\dagger a_{-,\sigma} + w_{+,\vec{k}}^\alpha a_{+,\sigma}^\dagger c_{\vec{k}\sigma} + w_{-,\vec{k}}^\alpha a_{-,\sigma}^\dagger c_{\vec{k}\sigma}). \tag{4.23}$$

which defines by comparison with Eq. (4.22) the coefficients $w_{\vec{k}\pm}^\alpha$ and $w_{\pm,\vec{k}}^\alpha$.

The structural similarity between Eqs. (4.9b) and (4.23) is quite apparent; this allows us to write immediately, purely by analogy to Eq. (4.15), that

$$\eta_{\text{c.m.}}^{\alpha\alpha} = \frac{1}{\pi M} \sum_\sigma \left(\Gamma_+^\alpha \frac{\Omega_+}{\epsilon_{+,\sigma}^2 + \Omega_+^2} + \Gamma_-^\alpha \frac{\Omega_-}{\epsilon_{-,\sigma}^2 + \Omega_-^2} - [(\Lambda_+^\alpha)^2 + (\Lambda_-^\alpha)^2] \frac{\Omega_+}{\epsilon_{+,\sigma}^2 + \Omega_+^2} \frac{\Omega_-}{\epsilon_{-,\sigma}^2 + \Omega_-^2} \right.$$
$$\left. + 2\Lambda_+^\alpha \Lambda_-^\alpha \frac{\epsilon_{+,\sigma}}{\epsilon_{+,\sigma}^2 + \Omega_+^2} \frac{\epsilon_{-,\sigma}}{\epsilon_{-,\sigma}^2 + \Omega_-^2} - (\Xi_+^\alpha)^2 \frac{\Omega_+^2 - \epsilon_{+,\sigma}^2}{\Omega_+^2 + \epsilon_{+,\sigma}^2} - (\Xi_-^\alpha)^2 \frac{\Omega_-^2 - \epsilon_{-,\sigma}^2}{\Omega_-^2 + \epsilon_{-,\sigma}^2} \right), \tag{4.24}$$

where we have used the definitions

$$\Xi_\pm^\alpha \equiv -\frac{1}{N} \operatorname{Im} \sum_{\vec{k}} \frac{w_{\vec{k}\pm}^\alpha V_{\pm,\vec{k}}}{\omega_+ - \epsilon_k}, \tag{4.25}$$

$$\Lambda_\pm^\alpha \equiv -\frac{1}{N} \operatorname{Im} \sum_{\vec{k}} \frac{w_{\vec{k}\mp}^\alpha V_{\pm,\vec{k}}}{\omega_+ - \epsilon_k}, \tag{4.26}$$

$$\Gamma_\pm^\alpha \equiv -\frac{1}{N} \operatorname{Im} \sum_{\vec{k}} \frac{|w_{\vec{k}\pm}^\alpha|^2}{\omega_+ - \epsilon_k}. \tag{4.27}$$

Having thus completed the derivation of analytic expressions for $\eta_{\text{rel}}^{\alpha\alpha}$ and $\eta_{\text{c.m.}}^{\alpha\alpha}$ we turn our attention to the numerical computation of our results, in order to obtain relevant physical information from our model; explicit forms for $\xi_\pm^\alpha$, $\lambda_\pm^\alpha$, $\gamma_\pm^\alpha$, $\Xi_\pm^\alpha$, $\Lambda_\pm^\alpha$, and $\Gamma_\pm^\alpha$ are provided in Appendix D.

V. NUMERICAL RESULTS AND DISCUSSION

In order to obtain numerical results one has to start with the solution of the self-consistency equations (B8′); use of Eq. (3.8) allows the self-consistency set to be recast into the form

$$\langle \hat{n}_{+,\sigma} \rangle = \frac{1}{\pi} \left[\arctan\left(\frac{\epsilon_{+,\sigma} + D}{\Omega_+} \right) - \arctan\left(\frac{\epsilon_{+,\sigma}}{\Omega_+} \right) \right], \tag{5.1a}$$

$$\langle \hat{n}_{-,\sigma} \rangle = \frac{1}{\pi} \left[\arctan\left(\frac{\epsilon_{-,\sigma} + D}{\Omega_-} \right) - \arctan\left(\frac{\epsilon_{-,\sigma}}{\Omega_-} \right) \right], \tag{5.1b}$$

where

$$\epsilon_{\pm,\sigma} = \epsilon_\pm + U_{\pm\pm} \langle \hat{n}_{\pm,-\sigma} \rangle + U_{+-} \langle \hat{n}_{\mp,-\sigma} \rangle + U'_{+-} \langle \hat{n}_{\mp,\sigma} \rangle. \tag{5.2}$$

It is well known that Eqs. (5.1) have two types of solutions: a nonmagnetic one, with $\langle \hat{n}_{\pm,\sigma} \rangle = \langle \hat{n}_{\pm,-\sigma} \rangle$; and magnetic solutions with $\langle \hat{n}_{\pm,\sigma} \rangle \neq \langle \hat{n}_{\pm,-\sigma} \rangle$. It can be checked that while nonmagnetic solutions always do exist, magnetic solutions are only found for a limited set of values of the parameters ϵ_H and Γ (we recall that ϵ_H determines $\epsilon_\pm$ [Eq. (A1)] and Γ does the same with $\Omega_\pm$ [Eq. (3.7)]).

A. Nonmagnetic solutions

Results for the nonmagnetic case are displayed in Figs. 1–6; here, as throughout this paper, atomic units are used for the energies and lengths are given in units of the Bohr radius.

Figures 1 and 2 show results of the binding energy calculation and can be summarized as follows: the position and depth of the binding energy minimum depends on the strength of the coupling to the metal Γ and the interatomic distance between adatoms R. The larger the value of Γ the larger the value of R, for minimum binding energy; on the other hand, increasing Γ leads to shallower E_B-vs-R curves. When the atomic level lies near the Fermi level of the electron gas it is clearly seen that for $\Gamma = 0.1$ or larger, finite interatomic distances between adatoms are not favored; this result agrees with calculations carried out by Ying, Smith, and Kohn[18] using the density functional formalism. However, for smaller values

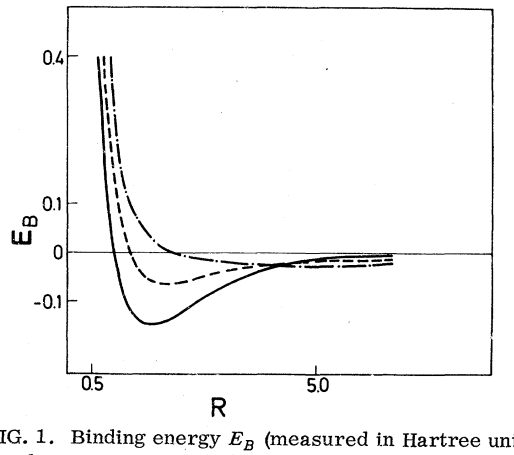

FIG. 1. Binding energy E_B (measured in Hartree units) vs nuclear separation R (in Bohr radius units), for the case when the atomic level ϵ_H is 0.5 below the Fermi level. The coupling Γ of the localized states to the metal states is 0.001 (solid line), 0.05 (dashed line), and 0.1 (dash-dot line).

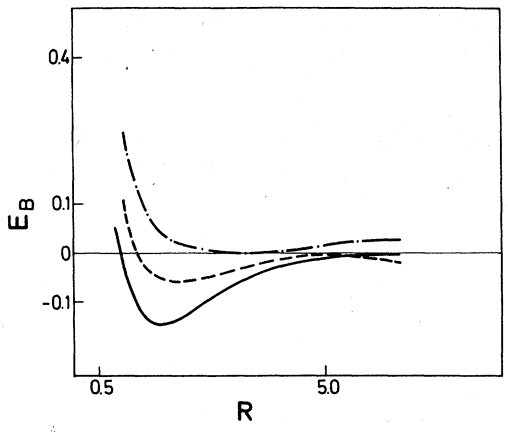

FIG. 2. Same as Fig. 1 but now the atomic level is 0.05 below the Fermi energy.

of Γ the adsorbed molecule seems to be favored compared to isolated adatoms.

For $\Gamma = 0.05$ we see in Fig. 2 oscillations in the binding energy E_B which are related to Friedel oscillations; for values of $\Gamma \geq 1$ these Friedel oscillations become much stronger and they may be responsible for overlayer structures, as found by Schrieffer and Einstein.[19] The general trends of our results are not affected by variations of the Fermi momentum k_F; the effect of changing k_F is only a quantitative variation of the position and depth of the minimum and in the amplitude of the Friedel oscillations. It can be stated that our results are in qualitative agreement with experiment; the weak coupling case can be interpreted as physisorption, while the strong coupling limit corresponds to chemisorption.

We now turn our attention to the friction coeffi-

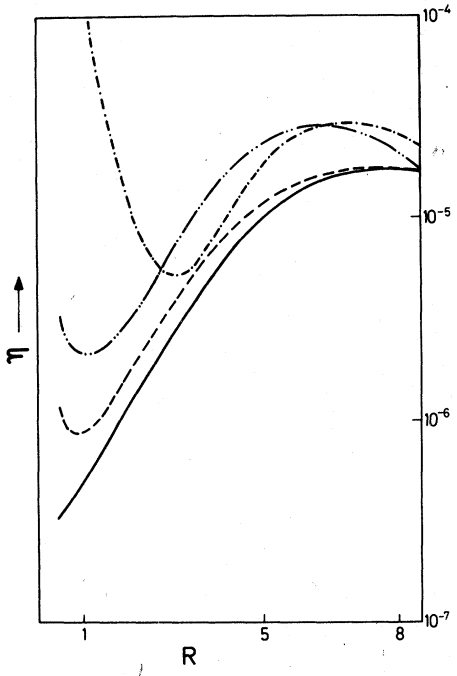

FIG. 3. Friction coefficient η, in units of $\hbar/a_0^2 M$, where M is the proton mass vs nuclear separation R. The atomic level is 0.5 below the Fermi energy and the coupling constant $\Gamma = 0.001$. The solid line corresponds to η^T_{rel}, the dashed line to $\eta^T_{\text{c.m.}}$, the dash-dot line to η^L_{rel}, and the dash–double-dot line to $\eta^L_{\text{c.m.}}$.

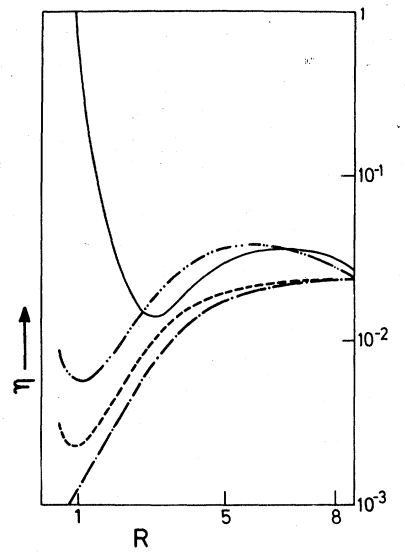

FIG. 4. Friction coefficient η vs nuclear separation R. The atomic level lies 0.5 below the Fermi energy and the coupling constant $\Gamma = 0.05$. The solid line corresponds to η^L_{rel}, the dashed line to $\eta^T_{\text{c.m.}}$, the dash-dot line to η^T_{rel}, and the dash–double-dot line to $\eta^L_{\text{c.m.}}$.

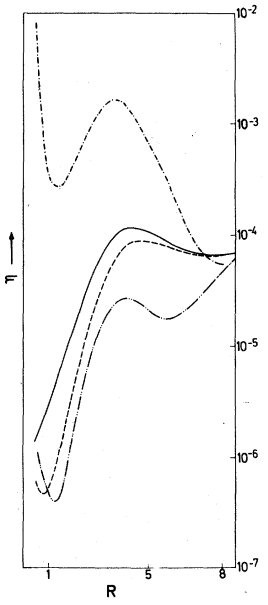

FIG. 5. Friction coefficient η vs nuclear separation R. The atomic level lies 0.05 below the Fermi energy and $\Gamma = 0.001$. The solid line corresponds to η^T_{rel}, the dashed line to $\eta^T_{\text{c.m.}}$, the dash-dot line to η^L_{rel}, and the dash–double-dot line to $\eta^L_{\text{c.m.}}$.

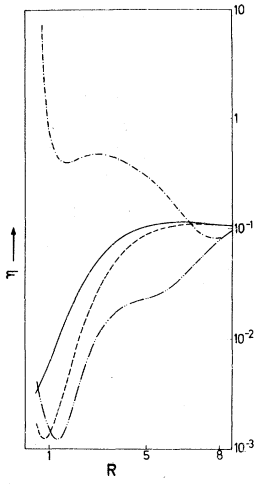

FIG. 6. Friction coefficient η vs nuclear separation R. The atomic level is 0.05 below the Fermi energy and $\Gamma = 0.05$. The solid line corresponds to η^{T}_{rel}, the dashed line to $\eta^{T}_{\mathrm{c.m.}}$, the dash-dot line to η^{L}_{rel}, and the dash–double-dot line to $\eta^{L}_{\mathrm{c.m.}}$.

cient results; η^{L}_{rel}, η^{T}_{rel} and $\eta^{L}_{\mathrm{c.m.}}$, $\eta^{T}_{\mathrm{c.m.}}$ (where L stands for longitudinal and T for transverse) have been evaluated by numerical computation of Eqs. (4.13)–(4.15) and (4.24), while expressions for the quantities involved: $\xi^{\alpha}_{\pm}$, $\lambda^{\alpha}_{\pm}$, $\gamma^{\alpha}_{\pm}$ and $\Xi^{\alpha}_{\pm}$, $\Lambda^{\alpha}_{\pm}$, $\Gamma^{\alpha}_{\pm}$, are explicitly given in Appendix D.

The most striking and important result we have obtained is that both η_{rel} and $\eta_{\mathrm{c.m.}}$ vary over three or four orders of magnitude, as displayed in Figs. 3–6; this is an indication that, depending on the circumstances, the friction coefficient might change considerably the value of the reaction rate, with the implication that absolute rate theory [11] (ART) may not always be applicable, as was already suggested by Suhl and co-workers.[1,2]

For short interatomic distances η^{L}_{rel} is always several orders of magnitude larger than $\eta_{\mathrm{c.m.}}$, both for the longitudinal (L) and transverse (T) cases.

As far as the oscillations seen in the η-vs-R graphs (which are related to Friedel oscillations in the electron gas), is concerned, we note that they are smoothed out as the coupling Γ increases.

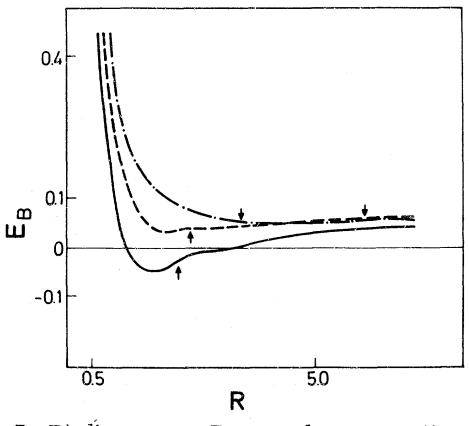

FIG. 7. Binding energy E_B vs nuclear separation R for the case when the atomic level ϵ_{H} lies 0.05 *above* the Fermi energy. The solid line corresponds to $\Gamma = 0.001$, the dashed line to $\Gamma = 0.05$, and the dash-dot line to $\Gamma = 0.1$. The arrows indicate where the magnetic solutions appear and disappear.

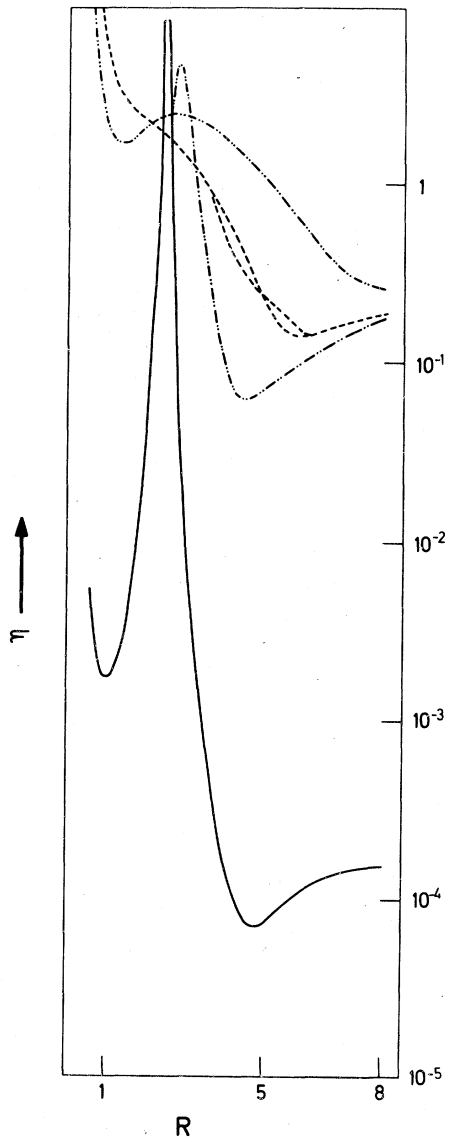

FIG. 8. Friction coefficient η^{L}_{rel} vs nuclear separation R, when the atomic level lies 0.05 above the Fermi energy. The solid line corresponds to $\Gamma = 0.001$, the dash–double-dot line to $\Gamma = 0.05$, and the dashed line to $\Gamma = 0.1$. For $\Gamma = 0.001$ only the magnetic solution has been plotted. For $\Gamma = 0.05$ the value of η for the stable magnetic solution shoots up at $R \cong 2.5$, while for $\Gamma = 0.1$ the magnetic value lies first below the unstable nonmagnetic value of η ($3.5 \lesssim R \lesssim 5$) and later above ($5 \lesssim R \lesssim 6$).

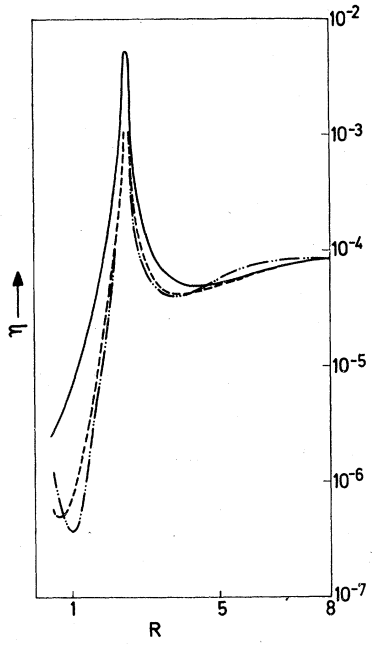

FIG. 9. Friction coefficient η vs nuclear separation R, when the atomic level lies 0.05 above the Fermi energy and $\Gamma = 0.001$. The solid line corresponds to η^T_{rel}, the dashed line to $\eta^T_{\text{c.m.}}$, the dash–double-dot line to $\eta^L_{\text{c.m.}}$. Only magnetic solutions are plotted.

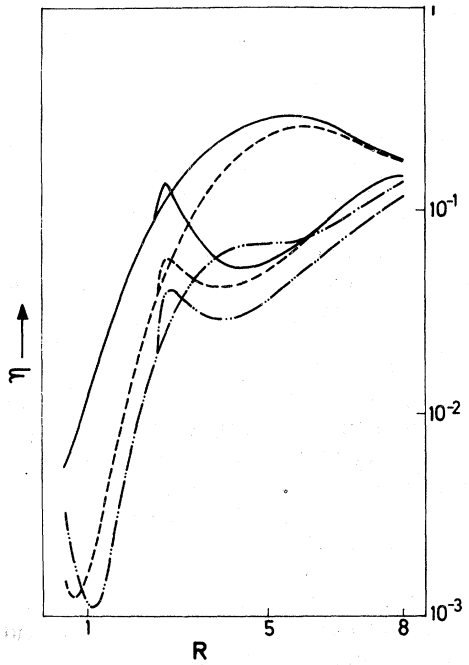

FIG. 10. Friction coefficient η vs nuclear separation R, when the atomic level lies 0.05 above the Fermi energy and $\Gamma = 0.05$. The magnetic (stable) values shoot up at $R = 2.5$. The solid line corresponds to η^T_{rel}, the dashed line to $\eta^T_{\text{c.m.}}$, and the dash–double-dot line to $\eta^L_{\text{c.m.}}$.

This smoothing of η can be understood in terms of the relation between the fricition coefficient and the curvature of $E_B(R)$, which becomes apparent after a careful inspection of the plotted curves. This way small changes in $E_B(R)$ may induce large variations in η_{rel}, as displayed in Fig. 3.

Another remarkable effect is the occurrence of a minimum in η_{rel} whenever energetic considerations favor the existence of an adsorbed molecule compared to two isolated adatoms.

B. Magnetic solutions

In Figs. 7–11 analogous results to the ones mentioned above are displayed; we simply focus now our attention on the changes brought about by the existence of magnetic solutions. Since the energy difference between the magnetic and nonmagnetic solution is tiny, we have only plotted the solution with lower energy and indicated with arrows the position R at which the magnetic solutions appear and disappear as R is increased.

In Fig. 7 it is seen that the curvature of E_B vs R changes drastically in the region where the transition from the nonmagnetic to the magnetic regime occurs; and, as expected, Fig. 8 shows a very large alteration in the values of η near these transition points, especially for small values of Γ. On the other hand, the behavior of the friction coefficient outside the transition region maintains the characteristics indicated in Sec. V A.

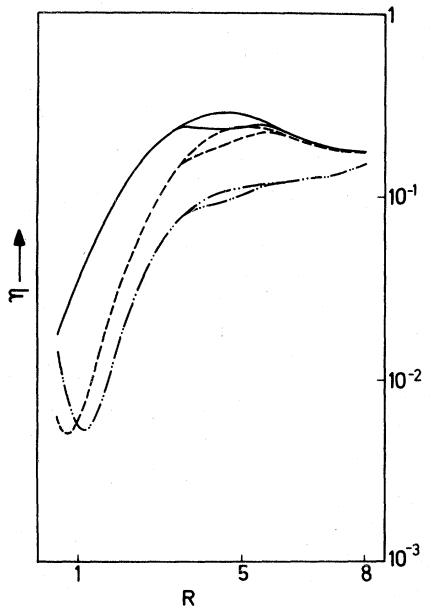

FIG. 11. Friction coefficient η vs nuclear separation R, when the atomic level lies 0.05 above the Fermi energy and $\Gamma = 0.1$. The magnetic (stable) values are the smaller ones in the region the curves are double valued. The solid line corresponds to η^T_{rel}, the dashed line to $\eta^T_{\text{c.m.}}$, and the dash–double-dot line $\eta^L_{\text{c.m.}}$.

Focusing our attention on the case $\Gamma = 0.05$ of Fig. 8 we observe that for small R the nonmagnetic solution is stable; as R increases the onset of the magnetic regime is accompanied by an increase of η, which rapidly turns downwards to a value at times more than a whole order of magnitude smaller than the (unstable) nonmagnetic value for η. For large values of R it seems that both solutions always merge.

Both the increase and the reduction of the value of η in the magnetic regime, relative to the nonmagnetic one, are sharp and large in the weak coupling case. As Γ increases the curves become smoother and the peaks broader. We should point out here that it is not clear whether or not these strong variations of η near the transition from the magnetic to the nonmagnetic regime are purely a consequence of the Hartree-Fock approximation. It should be mentioned that these results and the general trends discussed above constitute a natural extension and generalization of what we already reported[12] for the one-adatom case.

Summarizing, we state that our results strongly support the suggestion that ART is not always applicable to heterogeneously catalyzed reactions unless phonon effects, neglected here, return the friction value into the ART regime as recently suggested by Nozières,[20] and that in some cases dynamical effects (i.e., the details of the energy transfer mechanisms between catalyst and reacting particles) may contain the clue to why certain reactions take place over a specific substrate surface, while no reactions are catalyzed over an only slightly different one. It seems to us that purely structural considerations will not provide a complete understanding of the problem.

ACKNOWLEDGMENT

One of us (M.K.) would like to thank Professor P. Fulde for hospitality and support at the Max-Planck-Institute during the final stage of this work.

APPENDIX A: COULOMB INTEGRALS

In this appendix we provide explicit expressions for the parameters which appear in the term H_H of our Hamiltonian [Eq. (2.4)].

The energies of the bonding and antibonding states $|+\rangle$ and $|-\rangle$, respectively, are given by

$$\epsilon_\pm = \epsilon_H + (J+K)/(1\pm\Delta)\,, \tag{A1}$$

where

$$J = -\int \varphi_1^2(\vec{r})\,\frac{d^3r}{|\vec{r}-\vec{R}_2|} = -\frac{1}{R} + e^{-2R}\left(1+\frac{1}{R}\right)\,, \tag{A2}$$

$$K = -\int \varphi_1(\vec{r})\varphi_2(\vec{r})\,\frac{d^3r}{|\vec{r}-\vec{R}_2|} = -e^{-R}(1+R)\,, \tag{A3}$$

and

$$\Delta = \int \varphi_1(\vec{r})\varphi_2(\vec{r})\,d^3r = e^{-R}\,(1+R+\tfrac{1}{3}R^2)\,. \tag{A4}$$

Here, as throughout this paper, energies and distances are measured in Hartree and Bohr radius units, respectively; $\varphi_i(\vec{r})$ is the normalized $1s$ wavefunctions of the ith adatom and $R = |\vec{R}_1 - \vec{R}_2|$ is the separation between the nuclei of adatoms 1 and 2.

In terms of these and other similar parameters the Coulomb integrals are

$$\tilde{U}_{+-} = \int \frac{\varphi_+^2(\vec{r}_1)\varphi_-^2(\vec{r}_2)}{r_{12}}\,d^3r_1\,d^3r_2$$

$$= (U + J' - 2K')/[2(1-\Delta^2)]\,, \tag{A5}$$

$$\tilde{U}_{\pm\pm} = \int \frac{\varphi_\pm^2(\vec{r}_1)\varphi_\pm^2(\vec{r}_2)}{r_{12}}\,d^3r_1\,d^3r_2$$

$$= (U + J' + 2K' \pm 4L)/[2(1\pm\Delta)^2]\,, \tag{A6}$$

$$\tilde{U}'_{+-} = \tilde{U}_{+-} - \int \frac{\varphi_+(\vec{r}_1)\varphi_-(\vec{r}_2)\varphi_+(\vec{r}_2)\varphi_-(\vec{r}_1)}{r_{12}}\,d^3r_1\,d^3r_2$$

$$= (J' - K')/(1-\Delta^2)\,, \tag{A7}$$

$$U_{++--} = \int \frac{\varphi_+(\vec{r}_1)\varphi_+(\vec{r}_2)\varphi_-(\vec{r}_1)\varphi_-(\vec{r}_2)}{r_{12}}\,d^3r_1\,d^3r_2$$

$$= (U - J')/[2(1-\Delta^2)]\,, \tag{A8}$$

and

$$U_{+-+-} = U_{++--}\,. \tag{A9}$$

Here

$$U = \int \frac{\varphi_1^2(\vec{r}_1)\varphi_1^2(\vec{r}_2)}{r_{12}}\,d^3r_1\,d^3r_2 = \tfrac{5}{8}\,, \tag{A10}$$

$$J' = \int \frac{\varphi_2^2(\vec{r}_1)\varphi_1^2(\vec{r}_2)}{r_{12}}\,d^3r_1\,d^3r_2$$

$$= 1/R - e^{-2R}(1/R + \tfrac{11}{8} + \tfrac{3}{4}R + \tfrac{1}{6}R^2)\,, \tag{A11}$$

$$K' = \int \frac{\varphi_1(\vec{r}_1)\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\varphi_2(\vec{r}_2)}{r_{12}}\,d^3r_1\,d^3r_2$$

$$= \tfrac{1}{5}e^{-2R}(\tfrac{25}{8} - \tfrac{23}{4}R - 3R^2 - \tfrac{1}{3}R^3) + (6/5R)$$

$$\times \Delta^2(C + \ln R) + \Delta'^2\,\mathrm{Ei}(-4R) - 2\Delta\Delta'\,\mathrm{Ei}(-2R)]\,, \tag{A12}$$

$$L = \int \frac{\varphi_1(\vec{r}_1)\varphi_1^2(\vec{r}_2)\varphi_2(\vec{r}_1)}{r_{12}}\,d^3r_1\,d^3r_2$$

$$= e^{-R}(R + \tfrac{1}{8} + 5/16R)\,, \tag{A13}$$

and

$$\Delta' = e^R(1 - R + \tfrac{1}{3}R^2)\,, \tag{A14}$$

where the constant $C = 0.5772157\ldots$ is known as Euler's constant and

$$\mathrm{Ei}(x) = \int_{-\infty}^{x} \frac{e^t}{t}\, dt\,. \tag{A15}$$

APPENDIX B: GREEN'S FUNCTIONS

In this Appendix we solve the self-consistent set of equations for the Green's functions, used in Sec. III to calculate the binding energy and in Appendix C to obtain the correlation functions of Eq. (4.12), which in turn yields our result for the friction coefficient; the self-consistent solution we have obtained is valid in Hartree-Fock approximation.

We start from the definitions[14]

$$G^{\sigma}_{\vec{k}\vec{l}}(t) = \langle\langle c_{\vec{k}\sigma}(t) \,|\, c^{\dagger}_{\vec{l}\sigma}(0)\rangle\rangle, \tag{B1}$$

$$G^{\sigma}_{\pm,\vec{l}}(t) = \langle\langle a_{\pm,\sigma}(t) \,|\, c^{\dagger}_{\vec{l}\sigma}(0)\rangle\rangle, \tag{B2}$$

$$G^{\sigma}_{\pm\mp}(t) = \langle\langle a_{\pm,\sigma}(t) \,|\, a^{\dagger}_{\mp,\sigma}(0)\rangle\rangle, \tag{B3}$$

$$G^{\sigma}_{\pm\pm}(t) = \langle\langle a_{\pm,\sigma}(t) \,|\, a^{\dagger}_{\pm,\sigma}(0)\rangle\rangle, \tag{B4}$$

where

$$\langle\langle \hat{a}(t) \,|\, \hat{b}(0)\rangle\rangle = -i\Theta(t)\langle\{\hat{a}(t), \hat{b}(0)\}_{+}\rangle\,,$$

with $\Theta(t) = 1$ for $t > 0$ and 0 for $t < 0$ and $\{\hat{a}, \hat{b}\}_{+} = \hat{a}\hat{b} + \hat{b}\hat{a}$.

The equations of motion for these Green's functions read

$$G^{\sigma}_{\vec{k}\vec{l}}(\omega) = (\omega - \epsilon_k)^{-1}\{\delta_{\vec{k}\vec{l}} + [1/(N)^{1/2}](V_{\vec{k}+}G^{\sigma}_{+,\vec{l}} + V_{\vec{k}-}G^{\sigma}_{-,\vec{l}})\}\,, \tag{B5}$$

$$G^{\sigma}_{\pm,\vec{l}}(\omega) = \frac{1}{\omega - \epsilon^{\sigma}_{\pm}}\left(\frac{V_{\pm,\vec{l}}}{(N)^{1/2}}\,\frac{1}{\omega - \epsilon_l} + \sum_{\vec{k}} \frac{V_{\pm,\vec{k}}}{(N)^{1/2}}\,\frac{1}{\omega - \epsilon_k}\,\frac{V_{\vec{k}\pm}}{(N)^{1/2}}\,G^{\sigma}_{\pm,\vec{l}}\right), \tag{B6}$$

$$G^{\sigma}_{\pm\mp}(\omega) = \frac{1}{\omega - \epsilon^{\sigma}_{\pm}} \sum_{\vec{k}} \frac{V_{\pm,\vec{k}}}{(N)^{1/2}}\,\frac{1}{\omega - \epsilon_k} \times\left(\frac{V_{\vec{k},\pm}}{(N)^{1/2}}\,G^{\sigma}_{\pm\mp} + \frac{V_{\vec{k}\mp}}{(N)^{1/2}}\,G^{\sigma}_{\mp\mp}\right), \tag{B7}$$

$$G^{\sigma}_{\pm\pm}(\omega) = \frac{1}{\omega - \epsilon^{\sigma}_{\pm}}\left(1 + \sum_{\vec{k}} \frac{V_{\pm,\vec{k}}}{(N)^{1/2}}\,\frac{1}{\omega - \epsilon_k}\,\frac{V_{\vec{k}\pm}}{(N)^{1/2}}\,G^{\sigma}_{\pm\pm}\right), \tag{B8}$$

where

$$\epsilon^{\sigma}_{\pm} = \epsilon_{\pm} + U_{\pm\pm}\langle n_{\pm,\sigma}\rangle + U_{+-}\langle \hat{n}_{\mp,\sigma}\rangle + U'_{+-}\langle n_{\mp,\sigma}\rangle. \tag{B8'}$$

The average occupation numbers $\langle n_{\pm,\sigma}\rangle$ have to be determined self-consistently using the relation

$$\langle n_{\pm,\sigma}\rangle = \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega f(\omega)[G^{\sigma}_{\pm\pm}(\omega_{+}) - G^{\sigma}_{\pm\pm}(\omega_{-})]\,.$$

Equation (B6) directly yields

$$G^{\sigma}_{\pm,\vec{l}}(\omega) = \frac{1}{(N)^{1/2}}\,\frac{V_{\pm,\vec{l}}}{\omega - \epsilon_l}\left(\omega - \epsilon^{\sigma}_{\pm} - \frac{1}{N}\sum_{\vec{k}} \frac{|V_{\vec{k},\pm}|^2}{\omega - \epsilon_k}\right)^{-1}. \tag{B9}$$

Combination of Eqs. (B5) and (B9) gives

$$G^{\sigma}_{\vec{k}\vec{l}}(\omega) = \frac{1}{\omega - \epsilon_{\vec{k}}}\left[\delta_{\vec{k}\vec{l}} + \frac{1}{N}\,\frac{V_{\vec{k}+}V_{+,\vec{l}}}{\omega - \epsilon_l}\left(\omega - \epsilon^{\sigma}_{+} - \frac{1}{N}\sum_{k}\frac{|V_{\vec{k}+}|^2}{\omega - \epsilon_k}\right)^{-1} + \frac{1}{N}\,\frac{V_{\vec{k}-}V_{-,\vec{l}}}{\omega - \epsilon_l}\left(\omega - \epsilon^{\sigma}_{-} - \frac{1}{N}\sum_{\vec{k}}\frac{|V_{\vec{k}-}|^2}{\omega - \epsilon_k}\right)^{-1}\right]. \tag{B10}$$

Equation (B8) is also directly soluble and yields

$$G^{\sigma}_{\pm\pm}(\omega) = \left(\omega - \epsilon^{\sigma}_{\pm} - \frac{1}{N}\sum_{\vec{k}}\frac{|V_{\vec{k}\pm}|^2}{\omega - \epsilon_k}\right)^{-1}. \tag{B11}$$

Equation (B7) can be rewritten

$$\left(1 - \frac{1}{N(\omega - \epsilon^{\sigma}_{\pm})}\sum_{\vec{k}}\frac{|V_{\vec{k}\pm}|^2}{\omega - \epsilon_k}\right)G^{\sigma}_{\pm\mp}(\omega) = \frac{1}{N}\,\frac{1}{\omega - \epsilon^{\sigma}_{\pm}}\sum_{\vec{k}}\frac{V_{\vec{k}\mp}V_{\pm,\vec{k}}}{\omega - \epsilon_k}, \tag{B12}$$

but

$$\sum_{\vec{k}}\frac{V_{\vec{k}\mp}V_{\pm,\vec{k}}}{\omega - \epsilon_k} = \sum_{\vec{k}}\frac{1}{\omega - \epsilon_k}\,\frac{|V_{\vec{k},\vec{l}}|^2}{2(1 - \Delta^2)^{1/2}} \times(1 - e^{-i\vec{k}\cdot\vec{R}})(1 + e^{+i\vec{k}\cdot\vec{R}}), \tag{B13}$$

and the $\vec{k}$ integration is easily seen to vanish because of symmetry arguments; thus

$$G^{\sigma}_{\pm\mp}(\omega) = 0. \tag{B14}$$

APPENDIX C: CORRELATION FUNCTIONS

In this appendix we evaluate the correlation functions of our expressions for the friction coefficients [Eq. (4.12)], which provide explicit values for $\eta^{\alpha\alpha}_{\mathrm{rel}}$ and $\eta^{\alpha\alpha}_{\mathrm{c.m.}}$.

We start by considering

$$\langle \hat{I}^{\alpha}(0)\hat{I}^{\alpha}(t)\rangle = \sum_{s,\sigma}\{(W^{\alpha}_{++})^2\langle[\hat{n}_{+,s}(0) - \langle\hat{n}_{+,s}\rangle][\hat{n}_{+,\sigma}(t) - \langle\hat{n}_{+,\sigma}\rangle]\rangle + W^{\alpha}_{++}W^{\alpha}_{--}\langle[\hat{n}_{+,s}(0) - \langle\hat{n}_{+,s}\rangle][\hat{n}_{-,\sigma}(t) - \langle\hat{n}_{-,\sigma}\rangle]\rangle + W^{\alpha}_{--}W^{\alpha}_{++}\langle[\hat{n}_{-,s}(0) - \langle\hat{n}_{-,s}\rangle][\hat{n}_{+,\sigma}(t) - \langle\hat{n}_{+,\sigma}\rangle]\rangle + (W^{\alpha}_{--})^2\langle[\hat{n}_{-,s}(0) - \langle\hat{n}_{-,s}\rangle][\hat{n}_{-,\sigma}(t) - \langle\hat{n}_{-,\sigma}\rangle]\rangle\}, \tag{C1}$$

which in Hartree-Fock approximation reduces to

$$\langle \hat{I}^{\alpha}(0)\hat{I}^{\alpha}(t)\rangle = \sum_{s,\sigma} [(W^{\alpha}_{++})^2\langle a^{\dagger}_{s,+}(0)a_{\sigma,+}(t)\rangle\langle a_{s,+}(0)a^{\dagger}_{\sigma,+}(t)\rangle + (W^{\alpha}_{--})^2\langle a^{\dagger}_{s,-}(0)a_{\sigma,-}(t)\rangle\langle a_{s,-}(0)a^{\dagger}_{\sigma,-}(t)\rangle]. \tag{C2}$$

The cross terms, proportional to $W^{\alpha}_{+-}W^{\alpha}_{-+}$, do vanish since they are related to $G_{\pm\mp}(\omega)$ which is shown to be zero in Appendix B [Eq. (B14)].

The correlation functions in Eq. (C2) are evaluated through the use of thermal Green's functions, which by means of the formula[14]

$$\langle c^{\dagger}_j(0)c_i(t)\rangle = \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega\,[G_{ij}(\omega_+) - G_{ij}(\omega_-)]e^{-i\omega t}f(\omega), \tag{C3}$$

and

$$\langle c_i(0)c^{\dagger}_j(t)\rangle = -\frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega\,[G_{ij}(-\omega_+) - G_{ij}(-\omega_-)]e^{-i\omega t}f(\omega), \tag{C4}$$

where $f(\omega) = (e^{\beta\omega}+1)^{-1}$, yield the desired information. Thus, combination of (B2)–(B4) with (B11), and using the definition given by Eq. (14), gives

$$\int_0^{\infty} dt\,\langle \hat{I}^{\alpha}(0)\hat{I}^{\alpha}(t)\rangle = \frac{\beta}{2\pi^2}\int_0^{\infty} dt\int_{-\infty}^{\infty} d\omega\int_{-\infty}^{\infty} d\omega' f(\omega)f(\omega')e^{-i(\omega+\omega')t}Z(\omega,\omega'), \tag{C5}$$

where

$$Z(\omega,\omega') \equiv \sum_{\sigma}\left((W^{\alpha}_{++})^2\frac{\Omega_+}{(\omega-\epsilon_{+,\sigma})^2+\Omega_+^2}\,\frac{\Omega_+}{(\omega'+\epsilon_{+,\sigma})^2+\Omega_+^2} + (W^{\alpha}_{--})^2\frac{\Omega_-}{(\omega-\epsilon_{-,\sigma})^2+\Omega_-^2}\,\frac{\Omega_-}{(\omega'+\epsilon_{-,\sigma})^2+\Omega_-^2}\right). \tag{C6}$$

In the integrand of (C5) only the exponential factor is complex, thus

$$\begin{aligned}
\mathrm{Re}\int_0^{\infty} dt\,\langle \hat{I}^{\alpha}(0)\hat{I}^{\alpha}(t)\rangle &= \frac{\beta}{2\pi^2}\,\mathrm{Re}\int_0^{\infty} dt\int_{-\infty}^{\infty} d\omega\int_{-\infty}^{\infty} d\omega' f(\omega)f(\omega')e^{-i(\omega+\omega')t}Z(\omega,\omega')\\
&= \frac{\beta}{2\pi^2}\,\mathrm{Re}\int_0^{\infty} dt\int_{-\infty}^{\infty} d\omega\int_{-\infty}^{\infty} d\omega' f(\omega)f(\omega')e^{i(\omega+\omega')t}Z(\omega,\omega')\\
&= \frac{\beta}{4\pi^2}\,\mathrm{Re}\int_{-\infty}^{\infty} dt\int_{-\infty}^{\infty} d\omega\int_{-\infty}^{\infty} d\omega' f(\omega)f(\omega')e^{-i(\omega+\omega')t}Z(\omega,\omega').
\end{aligned}$$

Changing the order of integration it follows that

$$\mathrm{Re}\int_0^{\infty} dt\,\langle \hat{I}^{\alpha}(0)\hat{I}^{\alpha}(t)\rangle = \frac{\beta}{2\pi}\int_{-\infty}^{\infty} f(\omega)f(-\omega)Z(\omega,-\omega). \tag{C7}$$

Since $\beta f(\omega)f(-\omega) = -\partial f/\partial\omega$ we obtain through combination of Eqs. (4.12), (C6), and (C7), in the very-low-temperature limit, the result given in Eq. (4.13).

Following the same procedure, we derive in the Hartree-Fock approximation

$$\begin{aligned}
\langle \hat{I}^{\alpha}(0)\hat{J}^{\alpha}(t)\rangle + \langle \hat{J}^{\alpha}(0)\hat{I}^{\alpha}(t)\rangle = \frac{1}{(N)^{1/2}}\sum_{\sigma}\Bigg(& W^{\alpha}_{++}\langle a_{+,\sigma}(0)a^{\dagger}_{+,\sigma}(t)\rangle\sum_{\vec{k}}[W^{\alpha}_{+,\vec{k}}\langle a^{\dagger}_{+,\sigma}(0)c_{\vec{k},\sigma}(t)\rangle + W^{\alpha}_{\vec{k}+}\langle c^{\dagger}_{\vec{k},\sigma}(0)a_{+,\sigma}(t)\rangle]\\
&+ W^{\alpha}_{++}\langle a^{\dagger}_{+,\sigma}(0)a_{+,\sigma}(t)\rangle\sum_{\vec{k}}[W^{\alpha}_{+,\vec{k}}\langle c_{\vec{k},\sigma}(0)a^{\dagger}_{+,\sigma}(t)\rangle + W^{\alpha}_{\vec{k}+}\langle a_{+,\sigma}(0)c^{\dagger}_{\vec{k},\sigma}(t)\rangle]\\
&+ W^{\alpha}_{--}\langle a_{-,\sigma}(0)a^{\dagger}_{-,\sigma}(t)\rangle\sum_{\vec{k}}[W^{\alpha}_{-,\vec{k}}\langle a^{\dagger}_{-,\sigma}(0)c_{\vec{k},\sigma}(t)\rangle + W^{\alpha}_{\vec{k}-}\langle c^{\dagger}_{\vec{k},\sigma}(0)a_{-,\sigma}(t)\rangle]\\
&+ W^{\alpha}_{--}\langle a^{\dagger}_{-,\sigma}(0)a_{-,\sigma}(t)\rangle\sum_{\vec{k}}[W^{\alpha}_{-,\vec{k}}\langle c^{\dagger}_{\vec{k},\sigma}(0)a_{-,\sigma}(t)\rangle + W^{\alpha}_{\vec{k}-}\langle a^{\dagger}_{-,\sigma}(0)c_{\vec{k},\sigma}(t)\rangle]\Bigg),
\end{aligned} \tag{C8}$$

which, combined with Eqs. (A3) and (A4), yields

$$\langle \hat{I}^{\alpha}(0)\hat{J}^{\alpha}(t)\rangle + \langle \hat{J}^{\alpha}(0)\hat{I}^{\alpha}(t)\rangle = \sum_{\sigma}\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' f(\omega)f(\omega')e^{-i(\omega+\omega')t}$$
$$\times\Big(\{C^{\alpha}_{\sigma+}(\omega)+[C^{\alpha}_{\sigma+}(\omega)]^*\}W^{\alpha}_{++}(-i/2\pi)[G^{\sigma}_{++}(-\omega'_+)-G^{\sigma}_{++}(-\omega'_-)]$$
$$+\{C^{\alpha}_{\sigma+}(-\omega)+[C^{\alpha}_{\sigma+}(-\omega)]^*\}W^{\alpha}_{++}(i/2\pi)[G^{\sigma}_{++}(\omega'_+)-G^{\sigma}_{++}(\omega'_-)]$$
$$+\{C^{\alpha}_{\sigma-}(\omega)+[C^{\alpha}_{\sigma-}(\omega)]^*\}W^{\alpha}_{--}(-i/2\pi)[G^{\sigma}_{--}(-\omega'_+)-G^{\sigma}_{--}(-\omega'_-)]$$
$$+\{C^{\alpha}_{\sigma-}(-\omega)+[C^{\alpha}_{\sigma-}(-\omega)]^*\}W^{\alpha}_{--}(i/2\pi)[G^{\sigma}_{--}(\omega'_+)-G^{\sigma}_{--}(\omega'_-)]\Big)\,, \tag{C9}$$

where we have used the definition

$$C^{\alpha}_{\sigma\pm}(\omega)\equiv\frac{1}{(N)^{1/2}}\sum_{\vec{k}}W_{\vec{k}\pm}\frac{i}{2\pi}[G^{\sigma}_{\pm,\vec{k}}(\omega_+)-G^{\sigma}_{\pm,\vec{k}}(\omega_-)]\,. \tag{C10}$$

Substitution of our result for the Green's function [Eq. (B9)], above yields

$$C^{\alpha}_{\sigma\pm}(\omega)=\frac{\xi^{\alpha}_{\pm}}{\pi}\frac{\omega-\epsilon^{\sigma}_{\pm}}{(\omega-\epsilon^{\sigma}_{\pm})^2+\Omega^2_{\pm}}=[C^{\alpha}_{\sigma\pm}(\omega)]^*\,, \tag{C11}$$

where $\Omega_{\pm}$ and $\xi^{\alpha}_{\pm}$ were defined through Eqs. (4.16) and (4.17), respectively.

Combination of (C9), (C11), (B11), and Eq. (4.12), and using the same procedure we followed when evaluating $\langle \hat{I}^{\alpha}(0)\hat{I}^{\alpha}(t)\rangle$ above, we finally obtain the result given in Eq. (4.14).

The last correlation function we need to evaluate, written in Hartree-Fock approximation takes the form

$$\langle \hat{J}^{\alpha}(0)\hat{J}^{\alpha}(t)\rangle=\frac{1}{N}\sum_{\substack{\vec{k},\vec{k}'\\ \sigma}}\Big[W^{\alpha}_{\vec{k}+}W^{\alpha}_{+,\vec{k}'}\langle c^{\dagger}_{\vec{k}\sigma}(0)\,c_{\vec{k}',\sigma}(t)\rangle\langle a_{+,\sigma}(0)a^{\dagger}_{+,\sigma}(t)\rangle+W^{\alpha}_{+,\vec{k}}W^{\alpha}_{\vec{k}'+}\langle c_{\vec{k}\sigma}(0)c^{\dagger}_{\vec{k}'\sigma}(t)\rangle\langle a^{\dagger}_{+,\sigma}(0)\,a_{+,\sigma}(t)\rangle$$
$$+W^{\alpha}_{\vec{k}-}W^{\alpha}_{-,\vec{k}'}\langle c^{\dagger}_{\vec{k}\sigma}(0)c_{\vec{k}'\sigma}(t)\rangle\langle a_{-,\sigma}(0)a^{\dagger}_{-,\sigma}(t)\rangle+W^{\alpha}_{-,\vec{k}}W^{\alpha}_{\vec{k}'-}\langle c_{\vec{k}\sigma}(0)c^{\dagger}_{\vec{k}'\sigma}(t)\rangle\langle a^{\dagger}_{-,\sigma}(0)a_{-,\sigma}(t)\rangle$$
$$+W^{\alpha}_{\vec{k}+}W^{\alpha}_{\vec{k}'-}\langle c^{\dagger}_{\vec{k}\sigma}(0)a_{-,\sigma}(t)\rangle\langle a_{+,\sigma}(0)c^{\dagger}_{\vec{k}'\sigma}(t)\rangle+W^{\alpha}_{+,\vec{k}}W^{\alpha}_{-,\vec{k}}\langle c_{\vec{k}\sigma}(0)a^{\dagger}_{-,\sigma}(t)\rangle\langle a^{\dagger}_{+,\sigma}(0)c_{\vec{k}'\sigma}(t)\rangle$$
$$+W^{\alpha}_{\vec{k}-}W^{\alpha}_{\vec{k}'+}\langle c^{\dagger}_{\vec{k}\sigma}(0)a_{+,\sigma}(t)\rangle\langle a_{-,\sigma}(0)c^{\dagger}_{\vec{k}'\sigma}(t)\rangle+W^{\alpha}_{-,\vec{k}}W^{\alpha}_{+,\vec{k}'}\langle c_{\vec{k}\sigma}(0)a^{\dagger}_{+,\sigma}(t)\rangle\langle a^{\dagger}_{-,\sigma}(0)c_{\vec{k}'\sigma}(t)\rangle$$
$$+W^{\alpha}_{\vec{k}+}W^{\alpha}_{\vec{k}'+}\langle c^{\dagger}_{\vec{k}\sigma}(0)\,a_{+,\sigma}(t)\rangle\langle a_{+,\sigma}(0)c^{\dagger}_{\vec{k}'\sigma}(t)\rangle+W^{\alpha}_{+,\vec{k}}W^{\alpha}_{+,\vec{k}'}\langle c_{\vec{k}\sigma}(0)a^{\dagger}_{+,\sigma}(t)\rangle\langle a^{\dagger}_{+,\sigma}(0)c_{\vec{k}'\sigma}(t)\rangle$$
$$+W^{\alpha}_{\vec{k}-}W^{\alpha}_{\vec{k}'-}\langle c^{\dagger}_{\vec{k}\sigma}(0)\,a_{-,\sigma}(t)\rangle\langle a_{-,\sigma}(0)c^{\dagger}_{\vec{k}'\sigma}(t)\rangle+W^{\alpha}_{-,\vec{k}}W^{\alpha}_{-,\vec{k}'}\langle c_{\vec{k}\sigma}(0)a^{\dagger}_{-,\sigma}(t)\rangle\langle a^{\dagger}_{-,\sigma}(0)c_{\vec{k}'\sigma}(t)\rangle\Big]\,. \tag{C12}$$

Using again Eqs. (C3) and (C4) we obtain

$$\langle \hat{J}^{\alpha}(0)\hat{J}^{\alpha}(t)\rangle=\sum_{\sigma}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega' f(\omega)f(\omega')e^{-i(\omega+\omega')t}$$
$$\times\Big[-\frac{i}{2\pi}[G^{\sigma}_{++}(-\omega'_+)-G^{\sigma}_{++}(-\omega'_-)]B^{\alpha}_{\sigma+}(\omega)+\Big(\frac{i}{2\pi}[G^{\sigma}_{++}(\omega'_+)-G^{\sigma}_{++}(\omega'_-)]B^{\alpha}_{\sigma+}(-\omega)\Big)^*$$
$$-\frac{i}{2\pi}[G^{\sigma}_{--}(-\omega'_+)-G^{\sigma}_{--}(-\omega'_-)]B^{\alpha}_{\sigma-}(\omega)+\Big(\frac{i}{2\pi}[G^{\sigma}_{--}(\omega'_+)-G^{\sigma}_{--}(\omega'_-)]B^{\alpha}_{\sigma-}(-\omega)\Big)^*$$
$$+A^{\alpha}_{\sigma+}(\omega)A^{\alpha}_{\sigma-}(-\omega')+[A^{\alpha}_{\sigma+}(-\omega)\,A^{\alpha}_{\sigma-}(\omega')]^*+A^{\alpha}_{\sigma-}(\omega)A^{\alpha}_{\sigma+}(-\omega')+[A^{\alpha}_{\sigma-}(-\omega)A^{\alpha}_{\sigma+}(\omega')]^*$$
$$+C^{\alpha}_{\sigma+}(\omega)C^{\alpha}_{\sigma+}(-\omega')+[C^{\alpha}_{\sigma+}(-\omega)C^{\alpha}_{\sigma+}(\omega')]^*+C^{\alpha}_{\sigma-}(\omega)C^{\alpha}_{\sigma-}(-\omega')+[C^{\alpha}_{\sigma-}(-\omega)C^{\alpha}_{\sigma-}(\omega')]^*\Big]\,, \tag{C13}$$

where we used the definitions

$$A^{\alpha}_{\sigma\pm}(\omega)\equiv\frac{1}{(N)^{1/2}}\sum_{\vec{k}}W^{\alpha}_{\vec{k}\pm}\frac{i}{2\pi}[G^{\sigma}_{\mp,\vec{k}}(\omega_+)-G^{\sigma}_{\mp,\vec{k}}(\omega_-)]\,, \tag{C14}$$

$$B^{\alpha}_{\sigma\pm}(\omega)\equiv\frac{1}{N}\sum_{\vec{k},\vec{k}'}W^{\alpha}_{\vec{k}\pm}W^{\alpha}_{\pm,\vec{k}'}\frac{i}{2\pi}[G^{\sigma}_{\vec{k}'\vec{k}}(\omega_+)-G^{\sigma}_{\vec{k},\vec{k}}(\omega_-)]\,, \tag{C15}$$

while $C^{\alpha}_{\sigma\pm}(\omega)$ was defined through Eq. (C10). Substitution of (B9) in (C14) yields

$$A^{\alpha}_{\sigma\pm}(\omega)=\frac{\lambda^{\alpha}_{\mp}}{\pi}\frac{\omega-\epsilon^{\sigma}_{\mp}}{(\omega-\epsilon^{\sigma}_{\mp})^2+\Omega^2_{\mp}}\,. \tag{C16}$$

Substitution of (B10) in (C15) yields

$$B^{\alpha}_{\sigma\pm}(\omega)=\frac{1}{\pi}\left(\gamma^{\alpha}_{\pm}-\frac{(\lambda^{\alpha}_{\mp})^2\Omega_{\mp}}{(\omega-\epsilon^{\sigma}_{\mp})^2+\Omega^2_{\mp}}-\frac{(\xi^{\alpha}_{\mp})^2\Omega_{\pm}}{(\omega-\epsilon^{\sigma}_{\pm})^2+\Omega^2_{\pm}}\right),$$

where Ω, ξ, λ, and γ were defined in Eqs. (4.16)–(4.19), respectively. Combination of Eqs. (C13), (C16), (C17), (B8), and (4.12) yield finally Eq. (4.15), which completes the evaluation of the friction coefficient $\eta^{\alpha\alpha}_{\rm rel}$.

APPENDIX D: EXPLICIT FORMS OF THE PARAMETERS

In this appendix we provide explicit forms for the parameters $\xi^{\alpha}_{\pm}$, $\lambda^{\alpha}_{\pm}$, $\gamma^{\alpha}_{\pm}$, $\Xi^{\alpha}_{\pm}$, $\Lambda^{2}_{\pm}$, and $\Gamma^{\alpha}_{\pm}$, as well as the matrix elements $W^{\alpha}_{\pm\pm}$ and $W^{\alpha}_{\mp\pm}$, in terms of which the friction coefficients $\eta^{\alpha\alpha}_{\rm rel}$ and $\eta^{\alpha\alpha}_{\rm c.m.}$ are given. [See Eqs. (4.13)–(4.15) and Eq. (4.24).]

The estimation we carry out in this appendix is obtained by taking plane waves for the set $\{\vec{k}\}$ and 1s hydrogenlike orbitals for a_1 and a_2, while the potentials $V(\vec{r},\vec{R}_i)$ are taken to be Coulomb potentials.

A. Evaluation of $\vec{W}_{\pm\pm}$

With the assumptions stated before it is easy to prove that

$$-\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_1\rangle=+\langle a_2|\nabla_{\vec{r}}V(\vec{r},\vec{R}_1)|a_2\rangle \tag{D1}$$

and also

$$\begin{aligned}\langle a_2|\nabla_{\vec{r}}[V(\vec{r},\vec{R}_2)-V(\vec{r},\vec{R}_1)]|a_1\rangle&\\ =2\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_2\rangle&\\ =\langle a_1|\nabla_{\vec{r}}[V(\vec{r},\vec{R}_2)-V(\vec{r},\vec{R}_1)]|a_2\rangle\,.&\end{aligned} \tag{D2}$$

Thus

$$\begin{aligned}W_{\pm\pm}=[-2/(1\pm\Delta)][\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_1\rangle&\\ \pm\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_2\rangle]\,.&\end{aligned} \tag{D3}$$

The matrix elements above are now evaluated:

$$-\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_1\rangle=\frac{\alpha^3}{\pi}\int e^{-2\alpha|\vec{r}-\vec{R}_1|}\left(-\nabla_{\vec{r}}\frac{1}{|\vec{r}-\vec{R}_2|}\right)d^3r\,, \tag{D4}$$

where $\alpha=a_0^{-1}$ is the inverse Bohr radius. From now on we set $\alpha=1$, that is, we use atomic units. With the definition

$$\vec{R}=\vec{R}_2-\vec{R}_1 \tag{D5}$$

and, making $\vec{R}_1=0$, the matrix element of (D4) can be written

$$-\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_1\rangle=\frac{1}{\pi}\nabla_{\vec{R}}\int e^{-2r}\frac{1}{|\vec{r}-\vec{R}|}\,d^3r\,. \tag{D6}$$

In order to evaluate the integral it is convenient to use spheriodal coordinates (λ,μ,φ), where

$$\lambda\equiv(1/R)(r+|\vec{r}-\vec{R}|)\,, \tag{D7a}$$

$$\mu\equiv(1/R)(r-|\vec{r}-\vec{R}|)\,, \tag{D7b}$$

and

$$\int\int\int dx\,dy\,dz\cdots=\frac{R^3}{8}\int_0^{2\pi}d\varphi\int_{-1}^{1}d\mu\int_1^{\infty}d\lambda\,(\lambda^2-\mu^2)\cdots\,. \tag{D7c}$$

Thus

$$-\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_1\rangle=\frac{2\pi}{8\pi}\nabla_{\vec{R}}R^3\int_{-1}^{1}d\mu\int_1^{\infty}d\lambda\,(\lambda^2-\mu^2)e^{-R(\lambda+\mu)}\frac{2}{R}\frac{1}{\lambda-\mu}\,, \tag{D8}$$

$$-\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_1\rangle=(\hat{R}/R^2)[1-(1+2R+2R^2)e^{-2R}]\,. \tag{D9}$$

The other matrix element in Eq. (D3) for $W_{\pm\pm}$ is

$$-\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_2\rangle=\frac{1}{\pi}\int e^{-|\vec{r}-\vec{R}_1|}\left(-\nabla_{\vec{r}}\frac{1}{|\vec{r}-\vec{R}_2|}\right)e^{-|\vec{r}-\vec{R}_2|}\,d^3r\,, \tag{D10}$$

which with definition (D5) reduces to

$$-\langle a_1|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_2\rangle=\frac{-1}{\pi}\int e^{-(r+|\vec{r}-\vec{R}|)}\nabla_{\vec{r}}\left(\frac{1}{r}\right)d^3r\,, \tag{D11}$$

where now $\vec{R}_2=0$. Choosing the z axis along $\vec{R}$ the terms related to φ drop out, but we are required to know $\cos\theta$ in spheroidal coordinates. From

$$\vec{r}+|\vec{r}-\vec{R}|=\lambda R\,, \tag{D12}$$

it follows that

$$R(\lambda^2-2\lambda-1)=2r\cos\theta \tag{D13}$$

and thus

$$\cos\theta=(1+\lambda\mu)/(\lambda+\mu)\,. \tag{D14}$$

Combination of (D7), (D11), and (D14) yield

$$-\langle a_1|\nabla_r V(\vec{r},\vec{R}_2)|a_2\rangle = \vec{R}\int_1^\infty d\lambda e^{-R\lambda}\int_{-1}^1 d\mu \frac{\lambda-\mu}{(\lambda+\mu)^2}$$
$$= \vec{R}\int_1^\infty d\lambda e^{-R\lambda}\left[(3\lambda^2-1)\ln\left(\frac{\lambda+1}{\lambda-1}\right)-6\lambda\right]$$
$$= \vec{R}e^{-R}\int_0^\infty dx\, e^{-Rx}\left[(3x^2+6x+2)\ln\left(\frac{x+2}{x}\right)-6(x+1)\right]dx\ . \quad \text{(D15)}$$

These Laplace transforms can be handled and yield after a lengthy calculation

$$-\langle a_1|\nabla_r V(\vec{r},\vec{R}_2)|a_2\rangle = 2\vec{R}(e^{-R}/R^3)\left[(3+3R+R^2)\ln(2CR)-3R(2+R)-(3-3R+R^2)e^{2R}\,\mathrm{Ei}(-2R)\right], \quad \text{(D16)}$$

where C is the Euler-Mascheroni constant and $\mathrm{Ei}(x)$ was given by Eq. (A15). Substitution of (D9) and (D16) into (D3) completes the evaluation of $\vec{W}_{\pm\pm}$.

B. Evaluation of $\vec{W}_{\vec{k}\pm}$

We replace $\langle\vec{k}|\nabla_r V^{\mathrm{eff}}(\vec{r})|a_i\rangle$ by $\langle\vec{k}|\nabla_r V(\vec{r},\vec{R}_i)|a_i\rangle$; this approximation is reasonable except for $Ra_0 \sim 1$. Furthermore within the assumptions made above

$$-\langle\vec{k}|\nabla_r V(\vec{r},\vec{R}_2)|a_1\rangle = +\langle\vec{k}|\nabla_r V(\vec{r},\vec{R}_1)|a_2\rangle e^{i\vec{k}\cdot\vec{R}} \quad \text{(D17)}$$

and

$$\langle\vec{k}|\nabla_r V(\vec{r},\vec{R}_1)|a_1\rangle = \langle\vec{k}|\nabla_r V(\vec{r},\vec{R}_2)|a_2\rangle e^{i\vec{k}\cdot\vec{R}}\ . \quad \text{(D18)}$$

Thus there are only two independent matrix elements in Eq. (4.11), which we now evaluate:

$$\langle\vec{k}|\nabla_r V(\vec{r},\vec{R}_2)|a_1\rangle$$
$$= \frac{1}{(\pi)^{1/2}}\int e^{-i\vec{k}\cdot\vec{r}}\left(\nabla_r\frac{1}{|\vec{r}-\vec{R}_2|}\right)e^{-|\vec{r}-\vec{R}_1|}\,d^3r \quad \text{(D19)}$$

and, using again (D5) with $\vec{R}_1 = 0$,

$$-\langle\vec{k}|\nabla_r V(\vec{r},\vec{R}_2)|a_1\rangle$$
$$= \pi^{-1/2}\nabla_{\vec{R}}\int e^{-i\vec{k}\cdot\vec{r}}\frac{1}{|\vec{r}-\vec{R}|}e^{-r}\,d^3r\ . \quad \text{(D20)}$$

Defining

$$I_{\vec{k}}(R) \equiv \int e^{-i\vec{k}\cdot\vec{r}}\frac{e^{-r}}{|\vec{r}-\vec{R}|}d^3r\ , \quad \text{(D21)}$$

we obtain, using standard expansions for the plane waves and the denominator,

$$I_{\vec{k}}(R) = (4\pi)^{3/2}\sum_{l=0}^\infty \frac{i^l}{(2l+1)^{1/2}}\,Y_{l0}(\theta,\varphi)\left(\int_0^R \frac{r^{l+2}}{R^{l+1}}\,j_l(kr)e^{-r}\,dr + \int_R^\infty \frac{R^l}{r^{l-1}}\,j_l(kr)e^{-r}\,dr\right), \quad \text{(D22)}$$

where $j_l(z)$ is a spherical Bessel function and the coordinate system has been chosen with $\vec{k} = (-k_z, 0, 0)$ and $\vec{R} = (R,\theta,\varphi)$.

For our purposes the region of physical interest is when the distance between nuclei is larger than a Bohr radius; in that case the second integral in Eq. (D22) can be safely neglected. Moreover, since $k_F \sim a_0^{-1}$ the spherical Bessel function $j_l(kr)$ can be approximated by

$$j_l(z) \underset{z\to 0}{\longrightarrow} \frac{z^n}{(2n+1)!!}\ , \quad \text{(D23)}$$

where $(2n+1)!! = 1\times 3\times 5\times\cdots\times(2n+1)$. Then

$$I_{\vec{k}}(R) \cong (4\pi)^{3/2}\sum_{l=0}^\infty \frac{i^l}{(2l+1)^{1/2}}\,Y_{l0}(\theta,\varphi)\frac{k_F^l}{R^{l+1}}\frac{1}{(2l+1)!!}\int_0^R r^{2l+2}e^{-r}\,dr\ , \quad \text{(D24)}$$

which after some algebra yields

$$I_{\vec{k}}(R) \cong 4\pi\sum_{l=0}^\infty i^l P_l(\cos\theta)2^{l+1}(l+1)!\,(k_F R)^l R\sum_{j=0}^\infty \frac{R^j}{(2l+2+j)!}\ . \quad \text{(D25)}$$

Substitution of this last expression into (D20) finally gives

$$-\langle\vec{k}|\nabla_r V(\vec{r},\vec{R}_2)|a_1\rangle = -\pi^{-1/2}\sum_{l,j=0}^\infty i^l 2^{l+3}\frac{(l+1)!}{(2l+2+j)!}(k_F R)^l R^j\left((j+l+1)P_l(\cos\theta)\hat{R} + \frac{l}{\sin\theta}(\cos\theta P_l - P_{l-1})\hat{\theta}\right), \quad \text{(D26)}$$

and we recall that θ is the angle between the $\vec{R}$ and $\vec{k}$ vectors.

Next we evaluate the other distinct matrix element Eq. (D18), that is,

$$\langle\vec{k}|\nabla_{\vec{r}}V(\vec{r},\vec{R}_1)|a_1\rangle = -\pi^{-1/2}\int e^{-i\vec{k}\cdot\vec{r}}\left(\nabla_{\vec{R}_1}\frac{1}{|\vec{r}-\vec{R}_1|}\right)e^{-\alpha|\vec{r}-\vec{R}_1|}\,d^3r\,. \tag{D27}$$

Using again (D5) and making $\vec{R}_1=0$ we obtain

$$\begin{aligned}\langle\vec{k}|\nabla_{\vec{r}}V(\vec{r},\vec{R}_1)|a_1\rangle &= \pi^{-1/2}\int e^{-\vec{k}\cdot\vec{r}}\frac{\hat{r}}{r^2}e^{-r}\,d^3r\\ &= -\hat{k}4(\pi)^{1/2}i\int_0^\infty e^{-r}\,\frac{kr\cos kr-\sin kr}{(kr)^2}\\ &= i\hat{k}4(\pi)^{1/2}(1/k^2)(k-\tan^{-1}k)\,.\end{aligned} \tag{D28}$$

Substituting (D26) and (D28) in Eq. (4.11) we obtain

$$\begin{aligned}\vec{W}_{\vec{k}\pm} &= \hat{k}W_\pm(k)(1\mp e^{-i\vec{k}\cdot\vec{R}})\\ &\quad -[2/(2\pm2\Delta)^{1/2}]\langle k|\nabla_{\vec{r}}V(\vec{r},\vec{R}_2)|a_1\rangle(1\pm e^{-i\vec{k}\cdot\vec{R}})\,,\end{aligned} \tag{D29}$$

with

$$\hat{k}W_\pm(k)\equiv[-1/(2\pm2\Delta)^{1/2}]\langle\vec{k}|\nabla_{\vec{r}}V(\vec{r},\vec{R}_1)|a_1\rangle\,. \tag{D30}$$

After careful numerical analysis of the above expression in combination with Eqs. (D26), (D28), (D34), and (D41), it becomes apparent that the matrix element obtained in Eq. (D26) yields only a small contribution for small R, which decreases rapidly as R becomes larger; thus it can safely be neglected in the numerical computation as we have done throughout.

C. Evaluation of $\Omega_\pm$, $\xi^\alpha_\pm$, $\lambda^\alpha_\pm$, and $\gamma^\alpha_\pm$

We now evaluate the quantities defined in Eqs. (4.16)–(4.19) within the same approximations used above. Thus

$$\begin{aligned}V_{\vec{k}\pm} &= [1/(2\pm2\Delta)^{1/2}](V_{\vec{k}1}\pm V_{\vec{k}2})\\ &= [V_{\vec{k}1}/(2\pm2\Delta)^{1/2}](1\pm e^{-i\vec{k}\cdot\vec{R}})\,,\end{aligned} \tag{D31}$$

where

$$\begin{aligned}V_{\vec{k}1} &= \langle\vec{k}|V(\vec{r},\vec{R}_1)|a_1\rangle\\ &= \frac{1}{(\pi)^{1/2}}\int e^{-i\vec{k}\cdot\vec{r}}\,\frac{1}{|\vec{r}-\vec{R}|}\,e^{-|\vec{r}-\vec{R}_1|}\,d^3r\\ &= 4(\pi)^{1/2}e^{-i\vec{k}\cdot\vec{R}_1}/(1+k^2)\,.\end{aligned} \tag{D32}$$

Substitution of Eqs. (D31) and (D32) into Eq. (4.16) yields

$$\begin{aligned}\Omega_\pm &= -\frac{1}{N}\,\frac{8\pi}{1\pm\Delta}\,\mathrm{Im}\int d^3k\,\frac{2\pm2\cos\vec{k}\cdot\vec{r}}{(\omega_+-\epsilon_k)(1^2+k^2)^2}\\ &\cong \frac{16\pi^2}{1\pm\Delta}\left(1\pm\frac{\sin k_FR}{k_FR}\right)\frac{\rho(0)}{1^2+k_F^2}\,,\end{aligned} \tag{D33}$$

where $\rho(0)$ is the density of states at the Fermi level.

$\xi^\alpha_\pm$, $\lambda^\alpha_\pm$, and $\gamma^\alpha_\pm$ have three components ($\alpha=1,2,3$); but due to the cylindrical symmetry of our system only two of them are different and we denote them by L (longitudinal) and T (transverse).

Combination of Eqs. (4.17), (D29), and (D31) yields

$$\begin{aligned}\xi^L_\pm &\equiv -\frac{1}{N}\,\mathrm{Im}\sum_{\vec{k}}\frac{W^L_{\vec{k}\pm}V_{\pm,\vec{k}}}{\omega_+-\epsilon_k}\\ &= \frac{2\pi}{N}\,\mathrm{Im}\int_0^\infty dk\,k^2\,\frac{W_\pm(k)V_\pm(k)}{\omega_+-\epsilon_k}\\ &\qquad\times\int_{-1}^{1}(e^{-ikR\mu}-e^{ikR\mu})\mu\,d\mu\\ &\cong -2\pi\,\mathrm{Im}W_\pm(k_F)V_\pm(k_F)j_1(k_FR)\rho(0)\,,\end{aligned} \tag{D34}$$

where $V_\pm(k)$ is defined in analogy to (D30) as

$$V_\pm(k)\equiv\frac{4(\pi)^{1/2}}{(2\pm2\Delta)^{1/2}}\,\frac{1}{1+k^2}\,. \tag{D35}$$

As a consequence of cylindrical symmetry the azimuthal integrals vanish and thus

$$\xi^T_\pm = 0\,, \tag{D36}$$

$$\begin{aligned}\lambda^L_\pm &\equiv -\frac{1}{N}\,\mathrm{Im}\sum_{\vec{k}}\frac{W^L_{\vec{k}\mp}V_{\pm,\vec{k}}}{\omega_+-\epsilon_k}\\ &= \frac{2\pi i}{N}\int_0^\infty dk\,k^2\,\frac{W_\mp(k)V_\pm(k)}{\omega_+-\epsilon_k}\\ &\qquad\times\int_{-1}^{1}(2-e^{ikR\mu}-e^{-ikR\mu})\mu\,d\mu=0\,,\end{aligned} \tag{D37}$$

and a quite similar argument shows that

$$\lambda^T_\pm = 0\,. \tag{D38}$$

Now we turn our attention to

$$\begin{aligned}\gamma^L_\pm &\equiv -\frac{1}{N}\,\mathrm{Im}\sum_{\vec{k}}\frac{|W^L_{\vec{k}\pm}|^2}{\omega_+-\epsilon_k}\\ &= -\frac{2\pi}{N}\,\mathrm{Im}\int_0^\infty dk\,k^2\,\frac{|W_\pm(k)|^2}{\omega_+-\epsilon_k}\\ &\qquad\times\int_{-1}^{1}d\mu\,(2\mp e^{ikR\mu}\mp e^{-ikR\mu})\mu^2\\ &\cong\tfrac{1}{2}\pi|W_\pm(k_F)|^2L_\pm(k_FR)\rho(0)\,,\end{aligned} \tag{D39}$$

where $L_\pm(z)$ is given by

$$L_\pm(z)\equiv 4\{\tfrac{1}{3}\pm[(1/z)j_1(z)-j_2(z)]\}\,. \tag{D40}$$

Analogously

$$\gamma_{\pm}^{T} \equiv -\frac{1}{N}\,\mathrm{Im}\sum_{\vec{k}}\frac{|W_{k\pm}^{T}|^2}{\omega_+ - \epsilon_k}$$
$$= \frac{i}{N}\int_0^\infty dk\,k^2|W_\pm(k)|^2 \times\int_{-1}^{1} d\mu\,(2\mp e^{ikR\mu}\mp e^{-ikR\mu})(1-\mu^2) \times\int_0^{2\pi}\cos^2\varphi\,d\varphi$$
$$\cong \tfrac{1}{4}\pi|W_\pm(k_F)|^2\tilde{L}_\pm(k_FR)\rho(0)\ , \qquad \text{(D41)}$$

with

$$\tilde{L}_\pm(z) \equiv \tfrac{8}{3} \pm 4j_0(z) \mp 4[(1/z)j_1(z) - j_2(z)]\ . \qquad \text{(D42)}$$

D. Evaluation of $\Xi_\pm^\alpha$, $\Lambda_\pm^\alpha$, and $\Gamma_\pm^\alpha$

Now the quantities appearing in the expression for the center of mass friction coefficient are evaluated. Using the definition given in Eq. (4.23)

$$\Xi_{\pm}^{L} \equiv -\frac{1}{N}\,\mathrm{Im}\sum_{\vec{k}}\frac{w_{k\pm}^{L}V_{\pm,\vec{k}}}{\omega_+ - \epsilon_k}$$
$$= \frac{4\pi i}{N}\int_0^\infty dk\,k^2\,\frac{W_\pm(k)V_\pm(k)}{\omega_+ - \epsilon_k} \times\int_{-1}^{1}(1\pm\cos kR\mu)\,\mu\,d\mu = 0\ , \qquad \text{(D43)}$$

where we have used the relations given by Eqs. (4.22) and (4.23). Similarly

$$\Xi_{\pm}^{T} = 0\ , \qquad \text{(D44)}$$

since the azimuthal integrals vanish.

Next we consider

$$\Lambda_{\pm}^{L} \equiv -\frac{1}{N}\,\mathrm{Im}\sum_{\vec{k}}\frac{w_{k\mp}^{L}V_{\pm,\vec{k}}}{\omega_+ - \epsilon_k}\ , \qquad \text{(D45)}$$

which can be written

$$\Lambda_{\pm}^{L} = \frac{2\pi i}{N}\int_0^\infty dk\,k^2\,\frac{W_\pm(k)V_\mp(k)}{\omega_+ - \epsilon_k} \times\int_{-1}^{1}(e^{ikR\mu} - e^{-ikR\mu})\,\mu\,d\mu\ , \qquad \text{(D46)}$$

and by comparison with (D34) we have

$$\Lambda_{\pm}^{L} = -\frac{V_\mp(k_F)}{V_\pm(k_F)}\,\xi_{\pm}^{L} = -\frac{W_\pm(k_F)}{W_\mp(k_F)}\,\xi_{\mp}^{L}\ . \qquad \text{(D47)}$$

By the same token

$$\Lambda_{\pm}^{T} = 0\ . \qquad \text{(D48)}$$

Finally, using the same type arguments, we obtain

$$\Gamma_{\pm}^{L} = [\,|W_\pm(k_F)|^2/|W_\mp(k_F)|^2\,]\,\gamma_{\pm}^{L}\ , \qquad \text{(D49)}$$

and also

$$\Gamma_{\pm}^{T} = [\,|W_\pm(k_F)|^2/|W_\mp(k_F)|^2\,]\,\gamma_{\pm}^{T}\ . \qquad \text{(D50)}$$

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