Atomic force microscope as an open system and the Ehrenfest force

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(Received 12 January 1999; revised manuscript received 29 November 1999)

Two systems in contact, such as the tip of an atomic force microscope (AFM) and a sample, share a common surface. Each exerts an equal and opposite force on the other determined by the pressure it exerts on every element of the surface of separation, as required by the physics of an open system. In a quantum system, the force exerted on the tip is the Ehrenfest force, a force that is balanced by the pressure exerted on every element of its surface, as determined by the quantum stress tensor. The surface separating the tip from the sample is one of local zero flux in the gradient vector field of the electron density, the surface that separates two neighboring atoms. A zero-flux surface also defines a proper open system, one whose observables are governed by the equations of motion, the equation for the electronic momentum yielding the Ehrenfest force theorem. Thus the force measured in the AFM is exerted on a surface determined by the boundaries separating the atoms in the tip from those in the sample, and its response is a consequence of the atomic form of matter. This approach to the determination of the force measured in the AFM is contrasted with results reported in the literature that equate it to the Hellmann-Feyman forces exerted on the nuclei of the atoms in the tip.

FORCES AND OPEN SYSTEMS

In an atomic force microscope (AFM) a probe with a tip of atomic dimensions is attached to a cantilever whose deflections are measured as the tip scans the surface of a sample.[1] The force that causes the measured deflections is determined by the physics of an open system.[2,3] When two objects, such as the tip of an AFM and the object to be studied, are brought into contact they form a single system sharing a surface of separation. Each exerts an equal and opposite force on the other that is determined by the pressure each exerts on every element of the surface of separation. This description of the force acting on an open system in terms of the pressure acting on its surface is equally applicable to systems described by Newtonian or quantum mechanics. In the case of a quantum system, the force is termed the Ehrenfest force.[4] The properties of this force and its role in determining the mechanics of an open system are described here, with particular emphasis being placed on the interpretation of the force exerted on the tip of an AFM. This interpretation is contrasted with previous work in this area that equates this force to the Hellmann-Feynman forces[5] acting on the nuclei of the atoms in the tip, the force determined by the negative of the gradient of the potential energy of interaction between the tip and the sample.[6–12]

To make the distinction between the Hellmann-Feynman (HF) and Ehrenfest forces clear within the context of the AFM, consider pressing down with one's hand on a pencil, its tip on the surface of a desk, with the force $\mathbf{F}$. The desk exerts an equal and opposite force on the combined system of the pencil and hand. The HF force does not equal $\mathbf{F}$. Instead it measures the force $\mathbf{F}_\alpha$ required to displace the nucleus α of the atom in the tip of the probe, which is given by $\mathbf{F}_\alpha = -\nabla_\alpha E$. One is interested in the force not just on one nucleus of one atom in the tip of the probe, but rather in the force $\mathbf{F}$ that is exerted on the all of the atoms that make up the open system of ''pencil plus hand.'' This force is determined by the pressure exerted on every element of the surface S, separating the tip of the pencil from the desk. It is given by the expression $\mathbf{F} = -\oint d\mathbf{S} \cdot \boldsymbol{\sigma}$, where $\boldsymbol{\sigma}$ is the stress tensor. $\mathbf{F}$ is the force that the (cantilever) arm exerts on the attached spring, displacing it form its equilibrium position, the displacement measured in the AFM.

Inseparable from the definition of the force exerted on some object is the need to define a bounding surface on which the pressure is exerted. In a quantum system, the time rate of change of the average value of an observable $\hat{G}$ for an open system consists of two contributions: the average of the commutator $(i/\hbar)[\hat{H},\hat{G}]$, as found for a closed, isolated system and a surface term that measures the contribution from the flux in the current of $\hat{G}$ through the surface that the open system shares with its neighbors.[2,3] It is the surface flux contribution that distinguishes the physics of an open system from that of the total system and the definition of the surface is thus of paramount importance.

The surface enclosing an open system at the atomic level is uniquely defined.[2] It is a surface $S(\mathbf{r}_s)$ of local zero flux in the gradient vector field of the electron density, as described by

$$\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad \forall \ \mathbf{r} \in S(\mathbf{r}_s), \tag{1}$$

where $\mathbf{n}(\mathbf{r})$ is the unit vector normal to the surface. The zero-flux surface condition in Eq. (1), when imposed as a constraint in Schwinger's general variation of the action integral operator, extends his principle of stationary action to an open system.[13] Thus the observables of open systems bounded by surfaces satisfying Eq. (1) are described by the quantum-mechanical equations of motion and such systems are termed *proper open systems*. The equation of motion describing the Ehrenfest force is obtained by taking $\hat{\mathbf{G}} = \mathbf{p}$, the electronic momentum operator, and the resulting surface term describes the force exerted on an open system by its neighbor—the force exerted on the tip of an AFM by a surface, for example.

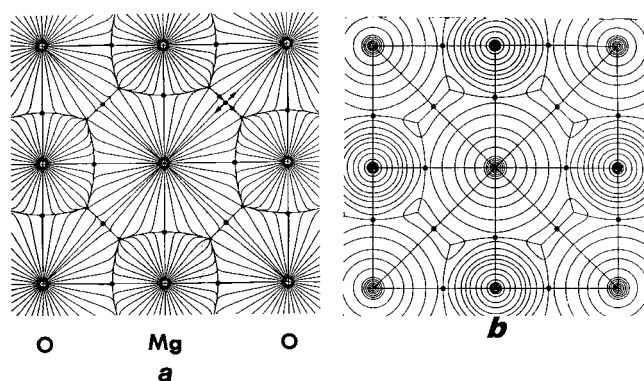PRB <u>61</u>   7795

FIG. 1. (a) Trajectories of $\nabla\rho(\mathbf{r})$ in the (100) plane of MgO. The region of space traversed by trajectories that terminate at a given nucleus where $\rho(\mathbf{r})$ is a local maximum, defines the atomic basin. Each basin is bounded by sets of trajectories that terminate at $(3,-1)$ or bond critical points (CP) denoted by dots. Only one pair of each set appears in this symmetry plane, as indicated by the pair of arrows for one O-O interaction. Also so indicated, is the unique pair of trajectories that originate at a bond CP and terminate, one each, at the neighboring nuclei and define the bond path. The density attains its maximum value in an interatomic surface and its minimum value along the bond path at a bond CP. (b) The total electron density in the same plane overlaid with the interatomic surfaces and bond paths defined by the trajectories associated with the bond CP's. Each Mg is linked by bond paths to six O atoms, while each O atom is in addition, linked by weaker interaction lines, to the 12 next-nearest O atoms. The density (in atomic units) increases in value from the outermost 0.001 contour inwards in steps of 2×10^{n}, 4×10^{n}, and 8×10^{n}, with n starting at -3 and increasing in steps of unity.

ATOMIC SURFACES

A necessary prelude to an application of the mechanics of an open system is a description of the form of the open systems defined by the condition of zero flux in Eq. (1). The electron density $\rho(\mathbf{r})$ exhibits a local maximum at the position of a nucleus. A consequence of this principal topological feature is that each nucleus acts as an attractor in the gradient vector field of the electron density and space is exhaustively partitioned into a disjoint set of mononuclear regions termed atomic basins.[2,14] Each basin is the region of space traversed by the set of trajectories of $\nabla\rho(\mathbf{r})$ that terminate at a given nucleus, as illustrated in Fig. 1(a) for a (100) plane in MgO. The interatomic surface of zero flux that separates the basins of two neighboring atoms is defined by a set of trajectories that terminate at a $(3,-1)$ critical point (CP), a point where $\nabla\rho(\mathbf{r})=\mathbf{0}$ and the Hessian of $\rho(\mathbf{r})$ exhibits one positive and two negative eigenvalues. The set of eigenvectors associated with the negative eigenvalues define the two-dimensional manifold that is the interatomic surface. The two unique eigenvectors associated with the single positive eigenvalue define a pair of trajectories of $\nabla\rho$ that originate at the CP and terminate at the neighboring nuclei, defining a line through space along which the density is a maximum. In the situation of electrostatic equilibrium, this line is termed a bond path. Thus atoms sharing an interatomic surface are bonded to one another,[15] an interpretation consistent with the observation that each bond path is mirrored by a virial path, a line of maximally negative potential energy density linking the same nuclei. Figure 1(b) illustrates the partitioning of the
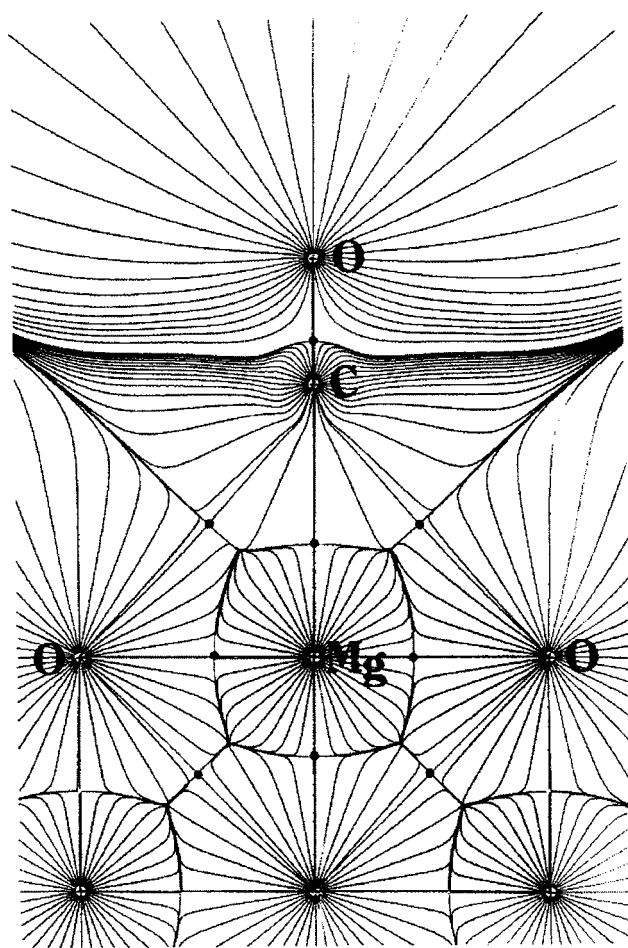

FIG. 2. Gradient vector field maps for a CO molecule bound to a Mg atom in the (100) surface of MgO. The C atom, which is to model the tip of CO viewed as a probe, is separated from the surface by five interatomic surfaces of zero flux, being linked to a Mg and four O atoms in the surface. The force exerted on the CO probe is a consequence of the pressure acting on each element of the five surfaces. The trajectories of $\nabla\rho(\mathbf{r})$ in the Mg basin that interact with and form the surface with C provide a representation of a ''dangling bond'' in the free surface, where they extend above the surface to infinity.

system into atoms obtained when the zero-flux surfaces defined by the gradient vector field are imposed on the density. Pendás and co-workers[16] have shown how the topological partitioning of densities in the solid state can be used to obtain a model-free classification and characterization of crystal structures.

The topological atoms have been identified with the atoms of chemistry because they recover the essential ideas associated with the atomic concept:[17] (a) the atomic properties, defined by the principle of stationary action, are characteristic and additive, summing to yield the corresponding values for the total system; (b) the properties of an atom are as transferable from one system to another as is the form of the atom in real space—if the density distribution of the atom is transferable, so are its properties.

Figure 2 portrays the atomic basins and interatomic surfaces defined by the gradient vector field of the electron density for a system consisting of a CO molecule bound to a Mg atom in a (100) surface of MgO. The reader is asked to

imagine the CO molecule to be the probe of an atomic force microscope and the MgO surface, the object under study. The surface of zero flux separating the tip from the atoms in the surface of the crystal consists of five interatomic surfaces, the carbon atom being linked by bond paths to the Mg atom and to four neighboring O atoms. One is free to choose any linked set of atoms as an open system and the C and O atoms of the probe are treated as a single open system. Any force exerted on the crystal by the probe is balanced by an equal and opposite force exerted on the probe by the crystal. The crystal exerts a pressure on every element of the surface, $d\mathbf{S}(\mathbf{r})$, a pressure determined by the quantum stress tensor $\boldsymbol{\sigma}(\mathbf{r})$. The integral of the resulting force $d\mathbf{S}(\mathbf{r}) \cdot \boldsymbol{\sigma}(\mathbf{r})$ over the zero-flux surface balances the Ehrenfest force on the probe. As the tip is moved across the crystal surface, the zero-flux surface, as determined by the atomic boundaries, changes and the probe responds to the change in its Ehrenfest force.

THE EHRENFEST ATOMIC FORCE THEOREM

The primal force theorem of an atomic system is obtained from the time rate of change of the electronic momentum, the Ehrenfest force theorem. Every property for a proper open system is defined in terms of a ''dressed'' density. This is a distribution in real space that replaces the property in question with a corresponding density that describes the interaction of a single electron with all of the remaining particles in the system, a consequence of the principle of stationary action for an open system. As a result, every property for the total system, including many-electron properties, is given by the sum of the atomic contributions.[2,3,18] The atomic force theorem obtained from the principle of stationary action for an open system for the observable $\mathbf{p}$ is expressed as

$$m \int_\Omega d\mathbf{r}\, \partial \mathbf{J}(\mathbf{r})/\partial t = N \int_\Omega d\mathbf{r} \int d\boldsymbol{\tau}' \Psi^*(-\boldsymbol{\nabla}_\mathbf{r}\hat{V})\Psi$$

$$+ \oint dS\, \boldsymbol{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}). \qquad (2)$$

Every observable yields an equation of similar form with the first term representing the time derivative of the property density, which in the present case is $m\mathbf{J}(\mathbf{r})$, the momentum density. The vector current $\mathbf{J}(\mathbf{r})$ in Eq. (2) is N times the single-particle electronic velocity density

$$\mathbf{J}(\mathbf{r}) = (\hbar/2mi)N \int d\tau' \{\Psi^*\boldsymbol{\nabla}_r\Psi - \boldsymbol{\nabla}_r\Psi^*\Psi\}. \qquad (3)$$

The symbol $N\int d\tau'$ denotes a summation over all spins followed by an integration over all electronic coordinates save those associated with the point $\mathbf{r}$, followed by multiplication by N. The application of this procedure to the product $\Psi^*\Psi$ yields the electron density $\rho(\mathbf{r})$. The integral on the left-hand side (LHS) of Eq. (2) gives the time rate of change of the electronic momentum over the open system Ω, thereby yielding the force acting on Ω. Equation (2) equates this to the forces exerted on the density within Ω by the total system, the first term on the right-hand side (RHS), and to the

pressure—the force per unit area—acting on each element of its bounding surface, the second term.

The first term comes from the atomic averaging of the commutator $(i/\hbar)[\hat{H},\mathbf{p}] = -\boldsymbol{\nabla}_\mathbf{r}\hat{V}$, where $\hat{H}$ is the many-particle Hamiltonian and $\hat{V}$ its potential energy operator. The operator $\mathbf{p} = -i\hbar\boldsymbol{\nabla}_\mathbf{r}$, the subscript $\mathbf{r}$ denoting the coordinate integrated over the open system. The commutator term yields the atomic average of the Ehrenfest force $\mathbf{F}(\mathbf{r},t)$ acting on the electron density at the point $\mathbf{r}$,

$$\mathbf{F}(\Omega,t) = \int_\Omega d\mathbf{r}\, \mathbf{F}(\mathbf{r},t) = \int_\Omega d\mathbf{r}\, N \int d\tau' \Psi^*(-\boldsymbol{\nabla}_\mathbf{r}\hat{V})\Psi,$$

$$(4)$$

an example of a dressed property density. The operator $-\boldsymbol{\nabla}_\mathbf{r}\hat{V}$ describes the force exerted on the electron at $\mathbf{r}$ by all of the remaining electrons and by the nuclei in the system, each of the particles being held fixed in some arbitrary configuration. The averaging of this operator implied by $\int d\tau'$ in Eq. (4) yields the force exerted on the electron density at $\mathbf{r}$ by the nuclei and by the average distribution of the remaining electrons in the entire system. Final integration over the atomic basin yields $\mathbf{F}(\Omega,t)$, the contribution to the force exerted on the total system from the basin forces acting in atom Ω. Thus the force, like all atomic properties, is additive.

The final term of Eq. (2) represents the contribution to the time derivative of $\mathbf{p}$ arising from the flux in its current density through the surface of the open system. It provides a measure of the force exerted on the open system arising from the flux in the momentum current density $\mathbf{J_p}(\mathbf{r})$. In Eq. (2), this ''momentum flux'' density is expressed in terms of the quantum stress tensor $\boldsymbol{\sigma}(\mathbf{r})$:[19]

$$-\{\mathbf{J_p}(\mathbf{r}) + \text{c.c.}\} = \boldsymbol{\sigma}(\mathbf{r}) = (\hbar^2/4m) \int d\tau' \{(\boldsymbol{\nabla}\boldsymbol{\nabla}\Psi^*)\Psi$$

$$-\boldsymbol{\nabla}\Psi^*\boldsymbol{\nabla}\Psi - \boldsymbol{\nabla}\Psi\boldsymbol{\nabla}\Psi^* + \Psi^*\boldsymbol{\nabla}\boldsymbol{\nabla}\Psi\}. \qquad (5)$$

The stress tensor has the dimensions of an energy density, that is, of a pressure or of a force per unit area and $d\mathbf{S}(\mathbf{r}) \cdot \boldsymbol{\sigma}(\mathbf{r})$ is the force exerted on an element of surface $d\mathbf{S}(\mathbf{r})$. The quantum stress tensor, first introduced by Schrödinger,[20] plays a dominant role in determining the local mechanics of the electron density and the properties of an open system. Since $\boldsymbol{\sigma}(\mathbf{r})$ is defined by a single-particle operator, it may be expressed in terms of the first-order density matrix, even though it determines the many-body forces operative in a molecule or solid.

The Ehrenfest force theorem, Eq. (2), is analogous to a basic postulate of classical continuum mechanics called the momentum principle.[21] This principle states that the time rate of change of the total momentum of a given set of particles forming a part Ω of some total system, equals the vector sum of all the external forces acting on the particles of the set, provided Newton's third law of action and reaction governs the forces. This statement of momentum balance leads to an equation that is term for term the analog of Eq. (2), with $m\mathbf{J}(\mathbf{r})$ replaced by the product of the mass and

velocity densities, the Ehrenfest force density by the classical body forces per unit volume, and the stress tensor by its classical analog.

In a stationary state, where the acceleration $\partial \mathbf{J}(\mathbf{r})/\partial t$ is zero and the system is in a state of static equilibrium, the Ehrenfest force $\mathbf{F}(\Omega)$ exerted on an open system Ω is balanced by the momentum flux density through its surface

$$\mathbf{F}(\Omega) + \oint d\mathbf{S}(\mathbf{r}_s) \cdot \boldsymbol{\sigma}(\mathbf{r}) = 0 \tag{6}$$

with a corresponding result for the classical case. Thus the force acting on an open system, quantum or classical, is determined by the *pressure exerted on each element of its surface*.[19]

The Ehrenfest force subsumes the response of all the components of an open system to the pressure exerted on its surface, of the nuclei as well as of the electron density, as demonstrated by the potential energy contributions obtained when one takes the virial of the Ehrenfest force. By setting $\hat{G}(\mathbf{r})$ in the principle of stationary action equal to the virial operator $\mathbf{r} \cdot \mathbf{p}$, one obtains the open system statement of the virial theorem.[2,3] For a stationary state the theorem takes the form

$$2T(\Omega) + \vartheta_b(\Omega) = -\vartheta_s(\Omega). \tag{7}$$

The two terms on the LHS—twice the electronic kinetic energy $T(\Omega)$ and the basin virial $\vartheta_b(\Omega)$—are obtained from the atomic average of the commutator of $\hat{H}$ with the virial operator. The atomic kinetic energy $T(\Omega)$ may be equivalently defined as $(1/2m)\langle \mathbf{p}^2 \rangle_\Omega$ or $(1/2m)\langle \mathbf{p} \cdot \mathbf{p} \rangle_\Omega$, because of the zero-flux surface condition. The basin virial $\vartheta_b(\Omega)$ is the average of the virial of the Ehrenfest force density, the quantity $\mathbf{r} \cdot \mathbf{F}(\mathbf{r}) = -\mathbf{r} \cdot \nabla \cdot \boldsymbol{\sigma}(\mathbf{r})$. The term on the RHS, the surface virial $\vartheta_s(\Omega)$, is determined by the flux in the current density of the virial operator through the atomic surface. It is the surface integral of the virial of the force exerted on unit surface area, the quantity $d\mathbf{S} \cdot \mathbf{r} \cdot \boldsymbol{\sigma}(\mathbf{r})$. The open system virial theorem is $-2T(\Omega) = \vartheta(\Omega)$, where $\vartheta(\Omega) = \vartheta_b(\Omega) + \vartheta_s(\Omega)$ is the total atomic virial. When $\vartheta(\Omega)$ is summed over all the atoms one obtains the total virial ϑ as given by

$$\vartheta = \sum_\Omega \vartheta(\Omega) = \langle \hat{V}_{en} \rangle + \langle \hat{V}_{ee} \rangle + \langle \hat{V}_{nn} \rangle + \sum_\alpha \mathbf{X}_\alpha \cdot \nabla_\alpha E$$

$$= \langle \hat{V} \rangle + \sum_\alpha \mathbf{X}_\alpha \cdot \nabla_\alpha E, \tag{8}$$

which satisfies the virial theorem for the total system, $-2T = \vartheta$. In Eq. (8), E is the total energy, $E = \langle \hat{T} \rangle + \langle \hat{V} \rangle$. Thus the virial of the Ehrenfest forces exerted on the electrons, in addition to yielding the electron-nuclear and electron-electron contributions to the potential energy, also contains the contributions from the nuclear-nuclear repulsion energy, and, if the system is not at electrostatic equilibrium, the virial of the external forces required to maintain a nonequilibrium geometry, the negative of the virials of the HF forces $-\nabla_\alpha E$ exerted on the nuclei. Thus the virial of the Ehrenfest force determines all of the contributions to the potential energy, including those that arise from the virial of any net HF forces exerted on the nuclei.
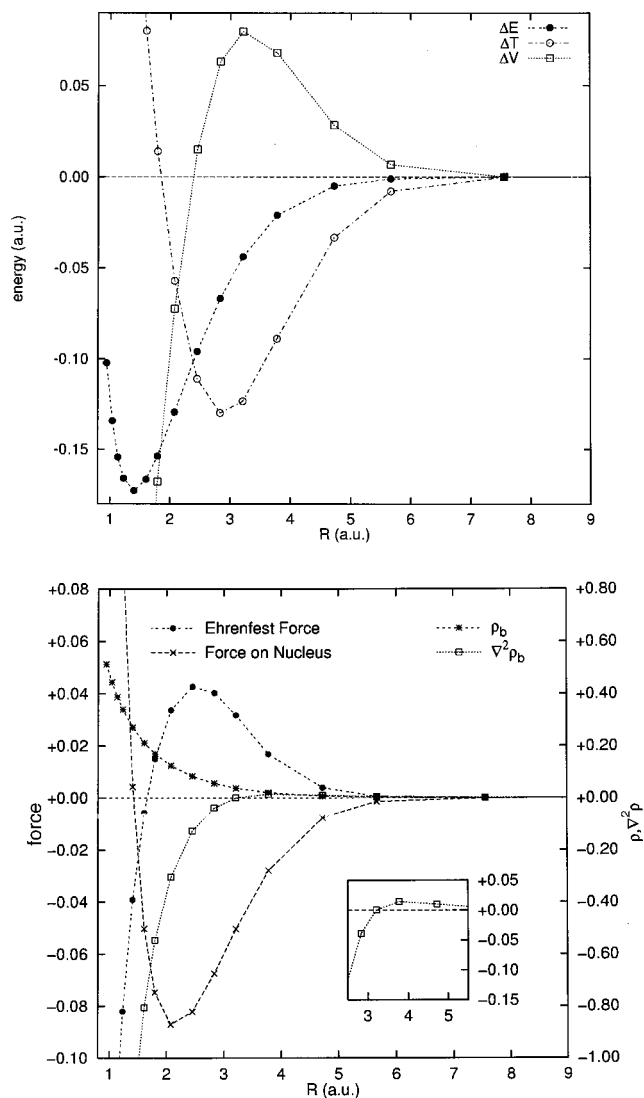

FIG. 3. (a) Plots of the changes in the total (E), kinetic (T), and potential (V) energies relative to the separated atoms in the formation of ground state H_2 ($^1\Sigma_g^+$). Internuclear separation R and energies in atomic units, 1 a.u.$=27.21$ eV. (b) Plots of the Ehrenfest force on a hydrogen atom, $\mathbf{F}(H)$, and of the Hellmann-Feynman force on a hydrogen nucleus as a function of R with the forces, measured in atomic units, on the LHS scale. 1 a.u.$=e^2/a_0^2=82.38$ nN. Also shown are the values of the electron density ρ_b and its Laplacian $\nabla^2 \rho_b$ at the bond critical point measured in atomic units on the RHS scale.

THE EHRENFEST FORCE AND MOLECULAR INTERACTIONS

Slater regarded the virial and Hellmann-Feynman theorems as "two of the most powerful theorems applicable to molecules and solids"[22] and for an open system, one must add to these the Ehrenfest force theorem. The virial theorem serves to relate the Ehrenfest and HF forces to the behavior of the total energy and its kinetic and potential energy contributions as a function of the separation between two open systems. The interrelation of these forces and energies is illustrated in Fig. 3 for the H_2 molecule as a function of the internuclear separation R. This simple system, which is amenable to an essentially exact description, is well suited to illustrate the three ranges of interactions encountered in the

use of the AFM, which, using the language of the relevant literature, are described as (a) the region of large separation where the overlap of the atoms is negligible and van der Waals attractive interactions are operative, (b) the region of overlap where ''covalent bond formation'' occurs, and (c) the region dominated by short-range repulsive forces. The present results are obtained from GAUSSIAN 94 (Ref. 23) using a $6\text{-}311^{++}G(2p,2d)$ basis in a configuration-interaction calculation [quadratic configuration interaction with all singles and doubles[24] (QCISD)] that yields a dissociation energy $D_e = 4.70$ eV (experimental value 4.75 eV) and an equilibrium separation $R_e = 1.40$ a.u. (experimental value 1.40 a.u.). In addition, the calculations incorporate self-consistent virial scaling (SCVS) of the electronic coordinates and they thus satisfy the virial theorem, $-2T = \vartheta$, to high accuracy at all separations.[25] The HF force is difficult to calculate because of the sensitivity of the force operator to small polarizations of the density in the vicinity of a nucleus. Thus the force calculated in terms of the nuclear gradient of the potential energy surface, $-\nabla_\alpha E$, does not in general equal the force calculated using the electrostatic theorem (the name applied to the generalized HF theorem when the parametric derivative of E is taken with respect to a nuclear coordinate) in which the force operator $-\nabla_\alpha \hat{V}_{ne}$ is averaged over the electron density and added to the nuclear force of repulsion. Even densities obtained from wave functions close to the Hartree-Fock limit do not satisfy the criterion of vanishing HF forces at a calculated energy minimum, yielding instead net forces of the order 7 nN for second-row nuclei.[26] In the present case, the HF force on a proton at R_e is calculated to be 0.35 nN = 0.0043 a.u.

In the case of a diatomic molecule, the virial of the external forces in Eq. (8) may be expressed as $R(dE/dR)$,[27] and the virial theorem itself may be written as

$$\Delta T = -\Delta E - R(dE/dR), \qquad (9)$$

where Δ denotes the difference in either T or E between the molecular value at a given separation R and the value for the separated atoms for which $T(\infty) = -E(\infty)$. Since the HF force vanishes at R_e, the virial theorem requires that T increase on bond formation and that the increase equal the magnitude of the decrease in the total energy; that is, $\Delta T(R_e) = -\Delta E(R_e) = -\frac{1}{2}V(R_e)$. However, the kinetic energy initially decreases on the approach of the two atoms, in the region of attractive forces preceding R_e, Fig. 3(a). An important point in demarking the regions of increase and decrease in T is the point R_i where the attractive HF force on a nucleus attains its maximum magnitude, corresponding to the inflection point on the $E(R)$ versus R curve,[2] Fig. 3(b). For H_2, the maximum force = 0.087 a.u. (= 7.2 nN) at $R \sim 2.1$ a.u. It is a general result that for $R \gg R_i$, T decreases and V increases relative to the separated atom values.[28] However, for $R \leq R_i$, T must increase and V decrease to eventually satisfy the requirements of the virial theorem that $\Delta T(R_e) = -\Delta E(R_e)$ and $\Delta V(R_e) = 2\Delta E(R_e)$ for a bound state. In general, $\Delta T(R)$ attains its minimum value at a separation slightly in excess of R_i, as found in Fig. 3(a) for H_2.

The hydrogen atoms in H_2 are defined by the planar interatomic surface generated by the trajectories of $\nabla\rho$ that terminate at the bond midpoint. The variation with R of the Ehrenfest force on one hydrogen atom, $\mathbf{F}(H)$, also exhibits an extremum as R is decreased, Fig. 3(b). It attains a maximum value of 0.043 a.u. (= 3.5 nN) for $R \sim 2.5$ a.u. at a separation slightly in excess of R_i. In this region where $\mathbf{F}(H) > \mathbf{0}$, the force on each atom is directed away from its neighbor. At a value of R slightly in excess of R_e, the direction of the force is reversed and each atom is drawn towards its neighbor. The force required to rupture a single covalent bond was recently measured in an AFM experiment by stretching the bond between two atoms, one being linked to the tip, the other to a surface.[29] If a H-H bond was so stretched when linked between the tip of an AFM and a surface, the measured force on the atom attached to the tip would be classed as attractive in the region where $\mathbf{F}(H) > \mathbf{0}$, since it would be opposing the force of the second atom drawing the hydrogen atom in the tip towards the surface; that is, the applied force would be one that pulled up on the tip. The bond would rupture when the force applied to the lever arm of the AFM was equal to the maximum value displayed by $\mathbf{F}(H)$ in Fig. 3(b). For shorter separations, where $\mathbf{F}(H) < \mathbf{0}$, the measured Ehrenfest force would be classed as repulsive, as it would be opposed by a force pushing against the interatomic surface it shares with its neighbor. The magnitude of the repulsive force increases rapidly as R is decreased past the point where $\mathbf{F}(H)$ changes sign. Thus the Ehrenfest force exerted on the tip of an AFM exhibits the characteristics of the force that is measured in an AFM: an initially attractive force as the tip approaches the surface of the sample that becomes increasingly repulsive on close approach of the tip to the sample.

The form of the $\mathbf{F}(H)$ curve versus the internuclear separation R shown in Fig. 3(b) for H_2 is found to be general for covalent and polar interactions. The $\mathbf{F}(\Omega)$ curves for N_2 and CO, obtained from multireference configuration-interaction calculations,[28] exhibit a maximum attractive force for $R > R_e$, which becomes repulsive at a separation just greater than R_e and increasingly repulsive for $R < R_e$. For example, the Ehrenfest force for N_2 exhibits a maximum of 14 nN at $R = 2.6$ a.u. a separation in excess of $R_e = 2.11$ a.u. The maximum HF force exerted on a nucleus as the bond is extended in N_2, determined from a Morse curve potential, equals 10 nN at $R = 2.5$ a.u., and the Ehrenfest force and the HF force are of similar magnitude, as found for H_2.

The LiF molecule is representative of an ionic interaction. The abrupt transfer of an electron from Li to F is complete by 10 a.u. resulting in net charges on the atoms of $\sim \pm 0.94e$ (Ref. 28) and the system corresponds to the approach of two closed-shell ions. Consequently, the electron and force densities exhibit low values in the interatomic surface and the Ehrenfest force curve does not exhibit a significant attractive maximum for $R > R_e$ as found for the covalent and polar interactions. However, it does exhibit the same steep decline in value for decreasing separations that begins as R approaches R_e and the two ions come into close contact. The value of the force at R_e equals 0.093 a.u., making it intermediate between the corresponding values for the covalent case of N_2, $|\mathbf{F}(N)| = 0.065$ a.u. and the polar interaction in CO, $|\mathbf{F}(C)| = |\mathbf{F}(O)| = 0.981$ a.u. The electron and nuclear contributions to $\mathbf{F}(\Omega)$ are detailed elsewhere,[28] but the ordering is readily understood. The valence density remaining on the C atom in the polar molecule CO, $q(C) = +1.2e$, is strongly polarized into its nonbonded region, a characteristic

feature of such an interaction and one that accounts for the near-zero dipole moment in the face of significant charge transfer. The force exerted on this density by the C nucleus is directed towards the interatomic surface and makes a significant contribution to $\mathbf{F}(C)$. In an ionic molecule, there is no remaining valence density on the cation, and the corresponding force exerted by the Li nucleus on the nearly spherical core density on Li is greatly reduced. In a covalent interaction the density is accumulated in the internuclear region and each nucleus draws its density away from the interatomic surface. Thus a polar interaction exhibits the largest repulsive Ehrenfest force on close approach of the two systems.

Experiments similar to the one describing the measurement of the force required to break an individual bond,[29] if applied to bonds representative of covalent, polar, and ionic interactions, should be capable of verifying the predicted ordering of the repulsive forces for close approach of the tip to the surface and the absence of a strong attractive force when the tip is bound to the surface by an ionic interaction.

COMPARISON WITH PREVIOUS CALCULATIONS

The contribution of van der Waals interactions to the measured force in an AFM experiment is generally equated to the appropriate gradient of the calculated energy.[9,11,12,30] At the atomic level, where a Lennard-Jones 6-12 potential is used to model the van der Waals potential energy of the nuclei, this procedure corresponds to calculating the HF force on the nuclei. However, in most applications, the van der Waals interaction between two surfaces is calculated using a continuum model that suppresses the atomic form of matter. Additivity of the (nonretarded) interactions between each atom in one surface with those in the other is generally assumed and the interactions are then proportional to the density of atoms in each surface. The final expression for the energy obtained in this manner is dependent upon the geometric shapes of the two surfaces, as expressed in terms of the Hamaker constant.[31] These models correspond to descriptions of the forces between macroscopic bodies and the force decays more slowly than the R^{-7} dependence describing the dispersion interaction between a pair of atoms,[31] the interaction between two planar surfaces, for example, behaving as R^{-3}.

In many applications a direct calculation of the energy of interaction of the tip and sample is undertaken using self-consistent field (SCF) procedures in the local-density approximation (LDA) form of density-functional theory or in pseudopotential calculations to model slabs. The tip is modeled by a single atom,[7,8] by a cluster,[8,10,11] or by slabs,[9] the latter being used to mimic a blunt tip close to a sample surface. Batra and co-workers[6–9] calculate the HF forces on the nucleus of the atom in the tip and on nuclei in the surface using the calculated electron density in the electrostatic form of the HF theorem. The force is incorrectly referred to as the ''force on the atom'' rather than on the nuclei,[6,9] the force on an atom being determined by the Ehrenfest force acting on the atomic surface.

In using SCF procedures to calculate the energy of interaction for the approach of a tip to a sample, one in effect is determining a reaction coordinate—the minimum energy of tip plus sample for each degree of separation—and one must

decide on a measure of separation between the tip and sample. In some cases this is taken to be the distance between the nucleus of the atom in the tip to one in the surface[7,8] and the force is equated to the HF force acting on the nucleus of the tip atom, a force that should be equal and opposite to the calculated forces exerted on the nuclei of the sample.[8] In other calculations a multiatom model of the tip is used. Shluger, Wilson, and Williams,[10] for example, model the tip using a silicate cluster capped with hydrogens, $Si_4O_{10}H_{10}$, with the Si atoms arranged in a tetrahedral manner and with a single Si-O-H silanol group perpendicular to the (001) surface of NaCl. The tip and a portion of the surface were treated as a cluster embedded in a slab to simulate the remainder of the crystal surface. For each separation of the silanol group above a cation or an anion site in the surface, as measured from the Si nucleus, the intervening O and H atoms of the silanol group and the atoms in the surface cluster were allowed to relax to new equilibrium geometries, and the force exerted on the tip was equated to the gradient of the energy with respect to the coordinates of the Si nucleus. In such a multiatom model of the tip, the calculated force depends upon the chosen reference nucleus.

The problems encountered when the force measured in the AFM is incorrectly identified with the HF force on a nucleus are not encountered when it is recognized that the description of the force exerted on the probe falls within the realm of the physics of an open system. The surface of zero flux separating the tip from the sample is present and defined at all separations of tip from sample, obviating the need to choose between which nucleus or nuclei are pertinent in a modeling of the system under study. The changes in the density that describe the changes in the nature of the interaction between tip and sample determine the changes in the form of the zero-flux surface, changes that in turn, through the stress tensor $\boldsymbol{\sigma}(\mathbf{r})$ equation (5), determine the changes in the force exerted on the tip. The physics of the interaction is inseparable from the topological changes in the density that accompany the approach of the tip to the sample. It is worth noting that the force measured in the AFM is exerted on a surface determined by the boundaries separating the atoms in the tip from those in the sample. Thus the response of the AFM is indeed a consequence of the atomic form of matter as displayed in real space by the charge distribution. The stress tensor $\boldsymbol{\sigma}(\mathbf{r})$ is determined by the first-order density matrix whose diagonal elements determine the density. A modeling of $\boldsymbol{\sigma}(\mathbf{r})$ in terms of the electron density in the surface would enable one to relate the measured force directly to the topographical features of the surface. Recent reviews indicate how the behavior of the electron density is governed by the local forms of the Ehrenfest force and the virial theorems obtained from the physics of an open system.[15,18]

MAGNETIC FORCE AND SCANNING TUNNELING MICROSCOPY

This section indicates how the physics of an open system can be used to describe the effects measured in magnetic force and scanning tunneling microscopy. The use of Schwinger's principle of stationary action to define the physics of an open system is applicable in the presence of an electromagnetic field,[32] thereby enabling an analysis of the

operation of the force microscope when used to measure ''electromagnetic forces,'' as first suggested by Binnig, Quate, and Gerber.[1] The principles and operation of the magnetic force microscope (MFM) are reviewed by Grütter, Mamin and Ruga.[33] The operation of the MFM is basically the same as that of the AFM, with the tip attached to a cantilever whose deflection changes in response to the atomic forces between the tip and surface. If the tip is approximated by a point dipole, the force $\mathbf{F}$ acting on the tip arising from the field $\mathbf{B}$ originating in the sample is, in the absence of currents, $\mathbf{F} = (\mathbf{m} \cdot \boldsymbol{\nabla})\mathbf{B}$ where $\mathbf{m}$ is the magnetic moment of the tip.

If the tip is treated as an open system, then the force exerted on it is generated by both mechanical and magnetic pressures exerted on the zero-flux surface separating it from the sample. For a system in a stationary state, the Ehrenfest force acting on the tip is given by the basin average of the commutator of the Hamiltonian and $\boldsymbol{\pi} = \mathbf{p} - (e/c)\mathbf{A}(\mathbf{r})$, the electronic momentum operator appropriate for a magnetic field. For an open system Ω, this force $\mathbf{F}(\Omega, \mathbf{B})$ is given by[2,32]

$$\mathbf{F}(\Omega, \mathbf{B}) = \langle -\boldsymbol{\nabla}\hat{V} \rangle_\Omega - (e/4mc)[\langle(\boldsymbol{\pi} \times \mathbf{B} - \mathbf{B} \times \boldsymbol{\pi})\rangle_\Omega + \text{c.c.}], \tag{10}$$

which, in addition to the field-free contribution given in Eq. (4) and denoted here by the symbol $\langle -\boldsymbol{\nabla}\hat{V} \rangle_\Omega$ contains a contribution from the interaction of the magnetic field with the electrons in the open system. These interior forces are balanced by corresponding mechanical and magnetic pressures acting on each element of the surface of the open system as given by

$$\mathbf{F}(\Omega, \mathbf{B}) = -\oint dS\, \boldsymbol{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) + (e/c)$$
$$\times \oint dS[\{\mathbf{A}(\mathbf{r})\mathbf{J}(\mathbf{r}) + \mathbf{J}(\mathbf{r})\mathbf{A}(\mathbf{r})\}$$
$$+ (e/mc)\rho(\mathbf{r})\mathbf{A}(\mathbf{r})\mathbf{A}(\mathbf{r})] \cdot \mathbf{n}(\mathbf{r}). \tag{11}$$

In addition to the mechanical force $dS(\mathbf{r})\boldsymbol{\sigma}(\mathbf{r})$, there are paramagnetic and diamagnetic contributions to the force exerted on the surface, the former involving the induced current $\mathbf{J}(\mathbf{r})$, the latter being proportional to the electron density. Grütter, Mamin, and Rugar[3] note that MFM images reflect both the topographic and magnetic structure of the sample. Equation (11) makes explicit the contribution of the mechanical and magnetic forces to the force exerted on the tip. As in the operation of the AFM, the form of the surface is itself determined by the atomic boundaries between the tip and sample. In the absence of a magnetic field, it is the relation between the stress tensor $\boldsymbol{\sigma}(\mathbf{r})$ and the density in the surface that relates the topology of the surface to the measured force.

The scanning tunneling microscope (STM) measures the ''tunneling current'' between tip and sample, brought into close proximity, that is induced by an applied field.[34]

Tersoff[35] has reviewed the theory underlying the calculation of the tunneling current. Present models use first-order perturbation theory to find the tunneling current proportional to the sum of the square of matrix elements that have the form of a flux in a current described by the mixing of two sets of nonorthogonal eigenstates from two different Hamiltonians, one for the tip and the other for the sample.[36] It would appear to be worthwhile to restate this problem using the physics of an open system, since it is the flux in property currents through the zero-flux surface that is unique to the physics of an open system and the tunneling current is then described in terms of the mixing of states of a single, total system.

CONCLUSIONS

There are many other problems that require the physics of an open system for their solution, as encountered for example, in attempts to calculate the pressure in a quantum system.[37] Past calculations, in analogy with the classical virial theorem for a contained gas of uniform density, incorrectly relate the pressure-volume product to the virial of the external forces of constraint, the ''wall forces.'' By assuming the system to be in some manner confined, one introduces a fictitious set of constraining forces separate from and in addition to those present in the system under consideration. The definition of pressure requires the existence of a surface upon which the pressure is exerted, thus placing the problem within the realm of the physics of an open system. An open system is confined by its environment and the pressure it experiences is that exerted on the zero-flux surface it shares with the atoms of the device that confine it. A scaling procedure demonstrates that the expectation value of the pressure-volume product of a proper open system is proportional to its surface virial,[37] $\vartheta_s(\Omega)$, Eq. (7). Thus the thermodynamic pressure is determined by the virial of the force resulting from the electronic momentum flux through its zero-flux surface, the same quantity that determines the Ehrenfest force acting on the open system. The pressure determined in this manner is a consequence of the mechanics of the interaction between the open system and the confining device.

The characterization of defects or impurities in solids and a determination of their contributions to the properties of a crystal also fall within the realm of the physics of an open system. The topology of the electron density defines the defect or impurity as an open system, separated from the atoms comprising the host crystal by a zero-flux surface. The properties of both guest and host are defined by the physics of proper open systems, an example being the recent characterization of the form and properties of an F center in an alkali halide crystal.[38]

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