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Properties of Atoms in Molecules: Caged Atoms and the Ehrenfest Force

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Abstract: This paper uses the properties of atom X enclosed within an adamantane cage, denoted by $X@C_{10}H_{16}$, as a vehicle to introduce the Ehrenfest force into the discussion of bonding, the properties being determined by the physics of an open system. This is the force acting on an atom in a molecule and determining the potential energy appearing in Slater's molecular virial theorem. The Ehrenfest force acting across the interatomic surface of a bonded pair atoms—atoms linked by a bond path—is attractive, each atom being drawn toward the other, and the associated surface virial that measures the contribution to the energy arising from the formation of the surface is stabilizing. It is the Ehrenfest force that determines the adhesive properties of surfaces. The endothermicity of formation for X = He or Ne is not a result of instabilities incurred in the interaction of X with the four methine carbons to which it is bonded, interactions that are stabilizing both in terms of the changes in the atomic energies and in the surface virials. The exothermicity for X = Be^{2+}, B^{3+}, and Al^{3+} is a consequence of the transfer of electron density from the hydrogen atoms to the carbon and X atoms, the exothermicity increasing with charge transfer despite an increase in the contained volume of X.

Introduction

Hydrocarbon complexes containing cage-centered atoms, termed endohedral atoms, have been synthesized and, as recently reviewed by Moran et al., are of both experimental and theoretical interest.[1] The smallest hydrocarbon cage complex so far synthesized was obtained by subjecting dodecahedrane $C_{20}H_{20}$ to a molecular beam of high energy He atoms.[2] The resulting cage complex, referred to as $He@C_{20}H_{20}$, is predicted to possess an energy 38 kcal/mol in excess of the isolated reactants.[3] Moran et al.,[1] in their theoretical study of endohedral hydrocarbon cage complexes, found that adamantane, $C_{10}H_{16}$, was the smallest cage capable of encapsulating a wide variety of endohedral atoms and ions, including H, He, Li^+, Be^{2+}, Mg^{2+}, and Ne. Of the $X@C_{10}H_{16}$ complexes, they found that only Be^{2+} gave an exothermic inclusion energy equal to −235.5 kcal/mol, the endothermicity of the other complexes ranging from 60 to 365 kcal/mol for X ranging from Li^+ to Ne.

The bonding in the cage complexes raises a number of interesting questions: a) What factors contribute to the stabilization of the complex? b) Do repulsive forces act within the complex, particularly between X and the carbons of the cage? c) In the endothermic complexes, is the excess energy stored in the interactions between X and the cage or among the atoms of the cage? These questions are answered unequivocally by the quantum theory of atoms in molecules, QTAIM, which describes an atom in a molecule using the physics of an open system.[4,5] This paper applies QTAIM to the adamantane complexes containing the endohedral atoms Be^{2+}, Li^+, He, Ne, and B^{3+}.

Computational Details

The virial theorem plays an important role in the physics of an open system, requiring that one employ wave functions wherein the electronic coordinates are scaled in a self-consistent manner. This is accomplished using a self-consistent virial scaling (SCVS) procedure written by Keith,[6] in conjunction with a Hartree−Fock (H−F) or extended H−F procedure. The calculations by Moran et al.[1] used B3LYP/6-31G(d) hybrid HF/DFT level of theory to account for the correlation necessary for the correct geometry predictions.

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Table 1. Total Energies (au), Binding Energies (kcal/mol), and $-V/T$ at MP2(full)/6-311++G(2d,2p)+SCVS, Together with the Integration Errors[a]

	MP2+SCVS	$-V/T$	$E - \sum_n E(n)$	$n - \sum_n N(n)$
adam	−389.91206	2.000030	0.37	0.0004
Be^{2+}@adam	−403.89214	2.000001	0.33	−0.0006
	(−223.17)			
Li$^+$@adam	−397.06746	2.000020	0.71	0.0017
	(70.20)			
He@adam	−392.55518	2.000022	0.80	0.0028
	(155.86)			
Ne@adam	−518.07666	2.000008	0.84	−0.0032
	(395.31)			
B^{3+}@adam	−413.22802	2.000008	0.91	−0.0006
	(−825.85)			
Al^{3+}@adam	−630.53887	2.000007	0.23	0.0023
	(−318.12)			

[a] Integration error in E in kcal/mol. The total energies for atoms in au: Be^{2+}(^{1}S), −13.62444; Li$^+$(^{1}S), −7.26729; He(^{1}S), −2.89150; Ne(^{1}S), −128.79456; B^{3+}(^{1}S), −21.99988; Al^{3+}(^{1}S), −240.11985; C(^{3}P), −37.77103; H(^{2}S), −0.49993.
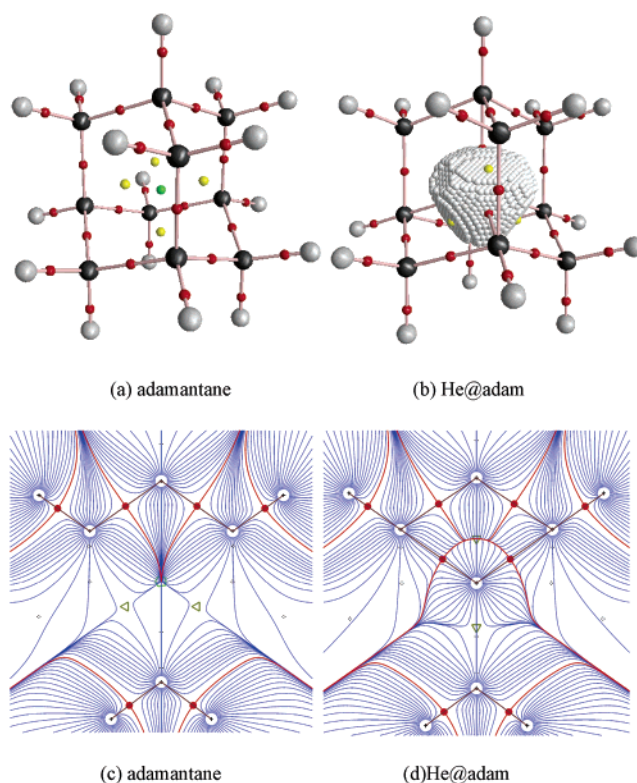
The present approach uses MP2(FULL) calculations, using GAUSSIAN98[7] which yield an equivalent description of the correlation, in conjunction with the SCVS procedure and employing the 6-311++G(2d,2p) basis set. The energy changes for the complex formation in the two approaches are comparable, the MP2/SCVS calculations yielding an exothermicity of formation for Be^{2+}@C$_{10}$H$_{16}$ 15 kcal/mol greater than the DFT result and an endothermicity of formation for He@C$_{10}$H$_{16}$ greater by 4 kcal/mol. The MP2 C−C and C−H bond lengths in adamantine are on the average 0.02 au shorter than the DFT values, using the smaller basis set. A B3LYP calculation using the present large basis set yields an endothermicity smaller by 2 kcal/mol and a C−C bond length greater by 0.023 au. The adamantane molecule and its complexes possess T_d symmetry, and none of the complexes exhibit imaginary frequencies.

The effect of the scaling of the electronic coordinates is to lower the total energies in amounts ranging from 0.0028 au for adamantane to 0.0036 au for Ne@C$_{10}$H$_{16}$. Table 1 lists the MP(full)/SCVS total energies of the separated atoms, of adamantane and of all of the complexes, together with ΔE, the energy of formation of the complexes with respect to the separated adamantane and X. Also listed are the $-V/T$ ratios together with the differences between the sum of the integrated energies and populations with the molecular values. The energy difference caused by the deviation of the calculated $-V/T$ ratios from the exact value of 2 equals 0.7 kcal/mol for the energy of Ne in Ne@C$_{10}$H$_{16}$, and the errors in the sums of the integrated energies and populations are acceptably small.

Definition of Molecular Structure

The quantum boundary condition for the definition of a *proper* open system is stated in terms of a surface $S(\mathbf{r})$ through which there is no flux in the gradient vector field of the density ρ, as expressed in eq 1[4]

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

(a) adamantane   (b) He@adam

(c) adamantane   (d) He@adam

Figure 1. Molecular graphs for adamantane (LHS) and He@C$_6$H$_{10}$. The He atom is shown bounded by its four interatomic surfaces. CPs are denoted by dots; red for bond, yellow for ring, and green for cage. The characteristic set [n,b,r,c] for each molecule satisfies the Poincarè-Hopf rule, n − b + r − c = 1. The lower diagrams are of the gradient vector fields of the electron density in σ_d symmetry planes with the same color scheme for the CPs. Bond paths are drawn in brown, and the intersections of the interatomic surfaces with the σ_d plane are shown in red. Two X|C1 and the two C1|C2 interatomic surfaces intersect at the upper ring CP in the diagram for He@C$_6$H$_{10}$, the atoms involved in one of the six four-membered rings.

The same boundary condition applies to the isolated molecule, a particular case of an open system, and the same equations of motion define the properties associated with an observable. In general the atomic surface $S(A)$ for atom A is composed of a number of interatomic surfaces $S(A|B)$, one for each bonded atom B. An interatomic surface is defined by the gradient vectors of ρ that *terminate* at a bond critical point (CP), ρ being a maximum in the surface at the CP. Thus ρ possesses two negative curvatures at the CP. The third curvature is positive, ρ being a minimum at the CP in a direction perpendicular to the surface yielding a (3,−1) CP. Two unique trajectories thus *originate* at the CP and terminate at each of the neighboring nuclei. They define a line along which the density is a maximum with respect to any neighboring line. In an equilibrium geometry of a bound state or within the attractive region of a potential well, the line is termed a *bond path*, and atoms so linked are bonded to one another and share a common interatomic surface.[8] The gradient vector fields for a σ_d symmetry plane in adamantane and in He@C$_{10}$H$_{16}$ are displayed in Figure 1 to show how the atomic boundaries and molecular structure

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are determined by the flow of trajectories in the associated gradient vector fields. One notes that the identification of an atom in a molecule as an open quantum system and the criterion for bonding are inseparable, both being physical consequences of the topology of the density displayed at a $(3,-1)$ or bond CP, a ubiquitous feature of charge distributions.[9]

A *molecular graph*, the linked network of bond paths, defines a system's molecular structure, as illustrated in Figure 1 for adamantane, a cage structure composed of 26 nuclei, 28 bond CPs, 4 ring CPs, and 1 cage CP, to give the characteristic set [26,28,4,1]. Each six-membered ring consists of alternating CH and CH_2 groups in a chair conformation. Also shown is the molecular graph for $He@C_{10}H_{16}$ wherein the cage CP is replaced by the He atom giving a structure with the characteristic set [27,32,6,0]. All of the adamantane complexes possess a structure homeomorphic with that for $He@C_{10}H_{16}$, one in which X is bonded to the four methine carbon atoms resulting in the formation of six bonded rings of atoms each consisting of X linked to two CH groups that are in turn bonded to a CH_2 group. The He atom is shown enclosed by its four interatomic surfaces that impart to it a tetrahedral shape. Its atomic boundary is totally enclosed within the cage, as is true for each of the X atoms.

The density exhibits a structural homeomorphism with the virial field, the field that determines the distribution of the potential energy density in real space. Thus the physical presence of bonding signifies an accompanying energetic stabilization, as every bond path in an energetically stable structure is mirrored by a *virial path*, a line linking the same nuclei along which the electronic potential energy density is maximally stabilizing.[10] Thus coexisting with every molecular graph, is a shadow graph—the virial graph—indicating the presence of a corresponding set of lines, again defined in real space, delineating the lowering in energy associated with the formation of the structure defined by the molecular graph. For a system close to a singularity, it is possible for the geometries at which the two fields cross a structural boundary to differ. The systems under study in the present paper are removed from any such singularities.

The properties of the density and energy density at the bond CPs are given in Table 2. The values of ρ_b, the density at the bond CP, for X|C1 are on the boundary of values that are characteristic of shared and closed-shell interactions. The Laplacian, $\nabla^2\rho_b$, is positive, characteristic of a closed-shell interaction, but the energy density, H_b is negative, characteristic of a shared interaction. The energy density equals the sum of the positive definite form of kinetic energy density $G(\mathbf{r}) > 0$ and the virial field $\mathcal{V}(\mathbf{r}) < 0$ at the CP, and, unlike a closed-shell interaction, it is not dominated by the kinetic energy as happens in the approach of two closed-shell systems. Thus the indices for the X|C1 interactions are intermediate between closed-shell and shared interactions and are, in this respect, similar to those found for bonding between metal atoms or between a metal atom and a ligand, as in the transition metal carbonyls, for example.[11,12] The indices for the adamantane cage atoms are as anticipated for shared interactions. The value of ρ_b decreases for C1|C2, as does the magnitude of $\nabla^2\rho_b$, when the cage is complexed,

Table 2. Bond Critical Point Data in Atomic Units and Delocalization Indices[a]

C1|X	ρ_b	$\nabla^2\rho_b$	H_b	$\delta(A,B)$
Be^{2+}	0.081	0.453	−0.024	0.081
Li^+	0.070	0.471	−0.004	0.077
He	0.081	0.382	−0.017	0.115
Ne	0.084	0.500	−0.009	0.168

C1|C2	ρ_b	$\nabla^2\rho_b$	H_b	$\delta(A,B)$
adam	0.240	−0.494	−0.188	0.824
Be^{2+}	0.201	−0.286	−0.131	0.806
Li^+	0.207	−0.323	−0.137	0.796
He	0.214	−0.370	−0.147	0.780
Ne	0.169	−0.206	−0.091	0.725

C1|H1	ρ_b	$\nabla^2\rho_b$	H_b	$\delta(A,B)$
adam	0.283	−1.030	−0.308	0.819
Be^{2+}	0.292	−1.140	−0.324	0.791
Li^+	0.294	−1.127	−0.325	0.820
He	0.284	−1.043	−0.308	0.824
Ne	0.284	−1.052	−0.307	0.833

C2|H2	ρ_b	$\nabla^2\rho_b$	H_b	$\delta(A,B)$
adam	0.280	−1.011	−0.303	0.824
Be^{2+}	0.290	−1.098	−0.316	0.810
Li^+	0.287	−1.064	−0.312	0.825
He	0.280	−1.014	−0.303	0.831
Ne	0.281	−1.026	−0.305	0.842

[a] C1 methine C and H1 its bonded H; C2 methylene C and H2 one of its bonded H.

with just the reverse occurring for the C1|H1 and C2|H2 interactions.

The delocalization index $\delta(A|B)$ measures the extent of the exchange of electrons between the basins of atoms A and B,[13] electrons that exchange being indistinguishable.[14] A value of unity implies the sharing of one Lewis pair, a value approached for the C|C and C|H interactions. Because of the delocalization of the electrons over other atoms in the molecule, the values fall short of the idealized values of unity obtained in a diatomic molecule. The indices were calculated from the natural orbitals obtained at the MP2 level using the procedure developed by Wang and Werstiuk.[15,16] The value of $\delta(X|C1)$ is greater for He and Ne than for Be and Li whose densities are contracted because of their positive charge, $+1.7e$ on Be and $+0.81e$ on Li. Both He and Ne possess density in excess of their closed-shell configurations, bearing charges of $-0.10e$ and $-0.11e$, respectively. The same double integration of the exchange density over the basins of two atoms, when weighted by the operator $-1/r_{12}$, determines the contribution of the exchange energy to the reduction in the Coulomb repulsion between the two atomic basins.[11,17] While the exchange between the basins of the X and C1 atoms is small, the reduction in the Coulomb repulsion between C1 and X is greatest for the He and Ne complexes.

The Ehrenfest, Feynman, and Virial Theorems

The electrostatic force, the only force operative in a field-free molecule, determines the potential energy operators in

the Hamiltonian. The resulting wave function enables one to determine the average electrostatic forces that act on the electrons and on the nuclei. The force acting on the electrons, the Ehrenfest force,[18] is obtained from the equation of motion for the electronic momentum operator $\hat{\mathbf{p}}$, while the force acting on a nucleus, the Feynman force,[19] is obtained from a corresponding equation for the nuclear gradient operator. Both forces contribute to the virial of the forces acting on the electrons as described by the virial theorem, the equation of motion for the virial operator $\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}$. The molecular virial theorem relates the virial of the Ehrenfest force acting on the electrons to their kinetic energy.[20] Thus through the Ehrenfest and Feynman theorems, one has the tools that are needed to describe the forces acting in a molecule and through the virial theorem, to relate these forces to the molecule's energy and its kinetic and potential contributions.

Ehrenfest Force Acting on an Atom

The Ehrenfest force determines the force acting on an entire atom in a molecule,[4] as opposed to the Feynman force, which acts only on its nucleus. The force acting over the body of an atom in a molecule—its basin—is, as for a classical open system, equal and opposite to the pressure acting on each element of its bounding surface. Thus it may be represented in terms of the surface integral of the quantum stress tensor, a quantum analogue of pressure. The quantum stress tensor was first introduced by Schrödinger in its relativistic form in 1927[21] and its properties discussed by Pauli in 1933, as described in his book.[22] While this force is balanced by equal and opposite surface forces exerted by the neighboring atoms in a stationary state, it is shown to be an important quantity in determining the attractive or repulsive nature of the interactions between atoms in a molecule, being particularly applicable to atoms enclosed within a molecular cage.

The Ehrenfest force is given by the equation of motion—the time rate-of-change—for $\hat{\mathbf{p}} = -i\hbar\nabla$, the momentum operator for an electron, yielding the force acting on the electron density in a proper open system A, eq 2[5,23,24]

$$m\int_A d\mathbf{r}(\partial\mathbf{J}/\partial t) = \int_A d\mathbf{r}\int d\tau'\Psi*(-\nabla_{\mathbf{r}}\hat{V})\Psi + \oint dS(A,\mathbf{r_s})\vec{\vec{\sigma}}(\mathbf{r})\mathbf{n}(\mathbf{r}) \quad (2)$$

An isolated molecule presents a special limiting case of the physics of an open system, one for which the surface integral in eq 2 vanishes. $\mathbf{J}$ is the vector current density, the momentum density divided by the electronic mass m and thus it is the electronic velocity. Its time derivative gives the electronic acceleration which, when multiplied by the mass, gives the force acting on the electrons in the atom. The first term on the RHS is the expectation value of the commutator $(i/\hbar)[\hat{H}, \hat{\mathbf{p}}]$ which equals the negative gradient of the full potential energy operator with respect to the coordinates of the electron at $\mathbf{r}$. The operator $-\nabla_{\mathbf{r}}\hat{V}$ determines the force exerted on the electron at $\mathbf{r}$ by all of the remaining electrons and the nuclei in fixed positions. By taking the expectation value of this force in the manner denoted by $N\int d\tau'$, that is, by summing over spins and integrating over the coordinates of all electrons but the one at $\mathbf{r}$, one obtains an expression for $\mathscr{F}(\mathbf{r})$, the force exerted

on an electron at position $\mathbf{r}$ by the *average distribution* of the remaining electrons and by the rigid nuclear framework—the force exerted on the electron density,[4]

$$\vec{\mathscr{F}}(\mathbf{r}) = N\int d\tau'\Psi*(-\nabla_r\hat{V})\Psi \quad (3)$$

the same integration procedure applied to $\Psi*\Psi$ determining the electron density $\rho(\mathbf{r})$. The force density $\vec{\mathscr{F}}(\mathbf{r})$, even though it involves two-electron interactions, is expressible as a density in real space, as found for all properties of a proper open system. Integration of $\vec{\mathscr{F}}(\mathbf{r})$ over atom A, as denoted by $\int_A d\mathbf{r}$ in eq 4, yields $\vec{\mathscr{F}}(A)$, the Ehrenfest force acting on the electron density over the basin of atom A. Eq 4 also indicates an alternative notation for the definition of an open system property.

$$\vec{\mathscr{F}}(A) = \int_A d\mathbf{r}\vec{\mathscr{F}}(\mathbf{r}) = 1/2\{(i/\hbar)\langle\psi,[\hat{H}, \hat{\mathbf{p}}]\psi\rangle_A + cc\} \quad (4)$$

The physics of an open system is distinguished by the presence of a surface contribution to the time rate-of-change of an observable $\widehat{\mathscr{O}}$, one that corresponds to the flux in the current density of $\widehat{\mathscr{O}}$ through the system's surface. Thus the final term on the RHS of eq 2 is the force exerted on the surface of the atom by the 'momentum flux density' that is expressed in terms of the quantum stress tensor, eq 5

$$\vec{\vec{\sigma}}(\mathbf{r}) = (\hbar^2/4m)\{(\nabla\nabla + \nabla'\nabla') - (\nabla\nabla' + \nabla'\nabla)\}\Gamma^{(1)}(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \quad (5)$$

where $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$ is the one-electron density matrix. The stress tensor has the dimensions of pressure, force/unit area (F/L^2), or energy density (E/L^3). The equation of motion for an open system given in eq 2 applies to any proper open system, including as a special limiting case, the total closed system for which the surface integral vanishes. In this case one obtains Ehrenfest's second relation, that $d\langle\hat{\mathbf{p}}\rangle/dt = \langle-\nabla\hat{V}\rangle = \langle\vec{\mathscr{F}}(\mathbf{r})\rangle$, and it is for this reason that $\vec{\mathscr{F}}(A)$ is identified as the Ehrenfest force acting on atom A. This force vanishes for a stationary state, and consequently, it has not played a role in discussions of the quantum mechanics of a total system. However, it is the dominant force in determining the mechanics of an open system, the physics of an atom in a molecule.

For a molecule in a stationary state, eq 2 reduces to

$$\vec{\mathscr{F}}(A) = -\oint dS(A;\mathbf{r_s})\vec{\vec{\sigma}}(\mathbf{r})\mathbf{n}_A(\mathbf{r}) = -\sum_{B\neq A}\oint dS(A|B;\mathbf{r_s})\vec{\vec{\sigma}}(\mathbf{r})\cdot\mathbf{n}_A(\mathbf{r}) = -\sum_{B\neq A}\vec{\mathscr{F}}(A|B) \quad (6)$$

and the force acting over the basin of the atom is equal and opposite to the force exerted on its surface $S(A)$. In general the atomic surface $S(A)$ in eq 6 is composed of a number of interatomic surfaces and the force on A may be correspondingly expressed as a sum of contributions $\vec{\mathscr{F}}(A|B)$, one from each interatomic surface $S(A|B)$ and where necessarily $\vec{\mathscr{F}}(A|B) = -\vec{\mathscr{F}}(B|A)$.

In a diatomic AB, the principal contributions to $\vec{\mathscr{F}}(A)$, the force on the density of atom A, are from the nucleus and the electrons of B, the nucleus of B exerting an attractive force and the electrons on B a repulsive one. The contribution to the Ehrenfest force exerted on the density of A by its

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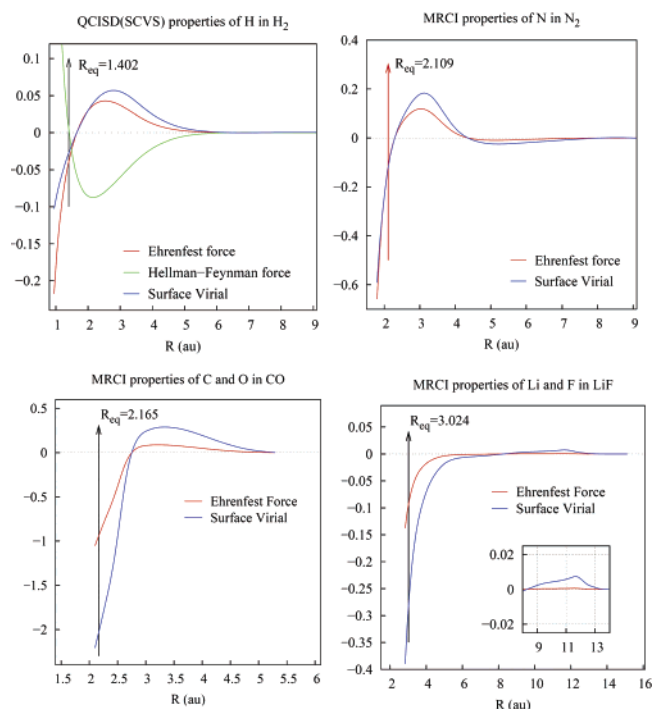
Figure 2. Variation of the Ehrenfest force $\vec{\mathcal{F}}(A)$, eq 4, and the surface virial $\mathcal{V}_s(A||B)$, eq 11, with internuclear separation R for H_2, N_2, CO, and LiF. QCISD denotes a wave function obtained from quadratic CI, including all singles and doubles, while MRCI denotes a multireference CI. All quantities are in atomic units. The equilibrium separation R_{eq} is indicated in each diagram. The Feynman force on a proton is also shown in the diagram for H_2. Note that $\vec{\mathcal{F}}(H)$ is maximally repulsive where the Feynman force is maximally attractive. The common zeroes in $\vec{\mathcal{F}}(A)$ and $\mathcal{V}_s(A||B)$ determine the ranges in R over which both quantities are repulsive and destabilizing or attractive and stabilizing, the latter occurring for separations greater than R_{eq}. Stabilization in the ionic system LiF occurs at a larger value of $R \sim 8$ au than for the shared or polar interactions. The transfer of charge from Li to F is essentially complete for $R < 10$ au.

own nucleus may be attractive or repulsive, that is, drawing it toward or away from B, depending upon the dipolar polarization of the density on A, and similarly for the intra-atomic electronic repulsion. The Ehrenfest force thus includes the electrostatic force exerted by the nuclei on the electron density, the attractive contribution to the Feynman force on the nuclei but not the contribution from the nuclear repulsive force, which in the case of $\vec{\mathcal{F}}(A)$ is replaced by the repulsions between the electrons. The behavior of $\vec{\mathcal{F}}(A)$ as a function of internuclear separation is illustrated in Figure 2 for H_2, N_2, CO, and LiF determined from highly correlated wave functions.[25] Table 3 gives the magnitudes of the Ehrenfest force acting on one of the atoms at R_e, which is attractive in each case, that is, the force on atom A is directed at atom B. The large value operative in CO is unique to polar, as opposed to shared or ionic bonding.

In general, for large separations in the approach of neutral atoms, $\vec{\mathcal{F}}(A) > 0$ and is repulsive, although it is slightly attractive for $R > 4.5$ au in N_2. The curves exhibit a maximum value—a maximum in the repulsion between the

Table 3. Ehrenfest Forces, Atomic Volumes, and Radii in Au[a]

AB	H_2	N_2	CO	LiF
$|\vec{\mathcal{F}}(A)|$	0.0395	0.0701	0.9788	0.0992

$X@C_{10}H_{16}$	Be^{2+}	Li^+	He	Ne
$|\vec{\mathcal{F}}(X)|$	0.1160	0.1099	0.1488	0.2171
$v(X)$	7.23	10.22	15.14	32.09
$\Delta R(C|C)$	0.159	0.145	0.118	0.370
$r_b(X)$	1.090	1.225	1.358	1.730
$r_b(C1)$	2.002	1.862	1.685	1.618

[a] $R(C|C) = 2.891$ au in adamantane.

two atomic basins—in the region of the inflection point in the potential energy curve, the point where the Feynman force is maximally attractive. For separations slightly greater than R_e, $\vec{\mathcal{F}}(A)$ undergoes a change in sign and a rapid decrease in value, and each atom experiences a force drawing it toward its neighbor. The increasingly attractive nature of $\vec{\mathcal{F}}(A)$ is the result of the accumulation of density in the binding region between the nuclei. The attraction of the nucleus external to A for the density of A is the principal stabilizing force in the formation of a molecule and its virial is the principal source of energy lowering. For example, in H_2, N_2, and CO at R_e, the largest single contribution to $\vec{\mathcal{F}}(A)$ is the attraction of the B nucleus for the density on A,[25] and the largest single contribution to the lowering of the energy in these molecules is the potential energy of interaction of the nucleus of one atom interacting with the density of the other.[11,25] The creation of attractive Feynman forces on the nuclei on the approach of two neutral atoms causes the potential energy to initially increase and the kinetic energy to decrease. Thus the curves for $V(R)$ versus R for H_2, N_2, and CO bear a similarity to the curves shown for corresponding behavior of $\vec{\mathcal{F}}(A)$ in terms of the values of R where they attain their maximum value and for which they change sign and become attractive.[25] In general, $\vec{\mathcal{F}}(A)$ parallels the potential energy of interactions between the atoms. For separations substantially less than R_e, the density on A will be increasingly polarized away from B causing both the electron−nuclear and electron−electron forces to make repulsive contributions to $\vec{\mathcal{F}}(A)$, and they, in conjunction with the electron−electron repulsion term for B, may result in the Ehrenfest force becoming repulsive. Because of the absence of the nuclear force of repulsion, this will occur for shorter distances than for the Feynman force, including the interactions between rare gas atoms.

The Ehrenfest force acting on the surface in LiF exhibits only a small repulsive increase for distances in excess of 12 au, becoming at first weakly and then strongly attractive as a result of the precipitous transfer of approximately one electron from Li to F that is essentially complete by 10 au, a picture in accord with the 'harpoon mechanism'. Thus in an ionic system, the attractive electrostatic interactions outweigh the repulsive ones following charge transfer.

Geometric Consequences of X Insertion and the Ehrenfest Force

The above introduction to $\vec{\mathcal{F}}(A)$ provides the necessary background for the discussion of the forces exerted on X

and its bonded methine carbon atoms caused by the insertion of X into the adamantane cage. A methine C atom and its bonded H are labeled C1 and H1, while a methylene carbon and a bonded H are labeled C2 and H2. The magnitude of the Ehrenfest force on atom X is given in Table 3 together with the volume of X, $v(X)$, the latter being a well-defined quantity as the X atoms are totally encased within the adamanatane cage. Also listed are the increases in the value of $R(C1|C2)$ from the value of 2.891 au in adamantane and the bonded radii $r_b(X)$ and $r_b(C1)$, the position of the X|C1 bond CP relative to the nuclei.

First and foremost, the Ehrenfest force on X is attractive in every case, drawing atoms X and C1 toward one another. As discussed below, the sign of $\overrightarrow{\mathcal{F}}(X|C1)$, the force exerted on the X|C1 surface, determines the sign of the surface virial, the contribution to the potential energy resulting from the formation of the X|C1 interatomic surface, and an attractive Ehrenfest force results in a stabilizing energy for the formation of the X|C1 surface. Surprisingly, the increase in $R(C1|C2)$ varies inversely with the volume of X for the first three members, becoming larger only for the insertion of the Ne atom whose volume is more than four times $v(Be)$. The increase in size of Li and He over Be is instead accommodated by a decrease in the bonded radius of C1, $r_b(C1)$. With the exception of its small reversal between the two ions, the magnitude of the attractive Ehrenfest force increases with the volume of X, increasing as the X|C1 bond CP moves closer to C1. Not only is there no Ehrenfest force of repulsion between the X and C1 atoms, its attractive nature increases with the size of the inserted atom, from Be^{2+} to He to Ne and the accompanying change from exothermicty to an increasing endothermicity with $v(X)$ does not have its origin in an increasing 'antibonding'[26] in the C1|X interaction. This behavior of the Ehrenfest force is reflected in the exceptional decrease in the energy of the X atoms, particularly He and Be, upon insertion and the conclusion is substantiated by the study of the energy changes of the individual atoms presented in a later section.

The Ehrenfest Force and the Interactions between Macroscopic Systems

The Ehrenfest force on the electron density plays a role that must be distinguished from the more familiar Feynman force acting on the nuclei. For example, for large separations between neutral atoms the Ehrenfest force is repulsive, whereas the Feynman forces are attractive, the former correctly reflecting the initial increase in the potential energy. The behavior of the two forces may be compared in Figure 2 for the hydrogen molecule. The Feynman force eventually vanishes at R_e and then becomes repulsive, while the Ehrenfest force becomes increasingly attractive, reflecting the decrease in the potential energy required by the virial theorem on bonding. The Feynman force is invoked in situations where the Ehrenfest force is in fact the operative force, these situations arising in cases that require the physics of an open system for their statement and solution. An example is the operation of the atomic force microscope (AFM).[27] The AFM and the surface under study are two components of a total system separated by a zero-flux

surface. It is the force transmitted from the tip of the probe to the attached cantilever arm of the AFM whose deflections are measured as the tip scans the surface of a sample. The force $\overrightarrow{\mathcal{F}}$ measured by the AFM is determined by the pressure that the sample exerts on each element of the surface of separation. The Feynman forced does not equal $\overrightarrow{\mathcal{F}}$. Instead, it measures the force $\mathbf{F}_\alpha$ required to displace the nucleus α of the atom in the tip of the AMF. One is interested in the force not just on the nucleus of one atom in the tip of the probe, but rather in the force $\overrightarrow{\mathcal{F}}$ that is exerted on all of the atoms that make up the open system "probe plus cantilever". This force is determined by the pressure exerted on every element of the surface separating the tip of the probe from the sample, as given in eq 6 in terms of the surface integral of the stress tensor. It is the Ehrenfest force $\overrightarrow{\mathcal{F}}$ that the cantilever arm exerts on the attached spring, displacing it from its equilibrium position, the displacement measured in the AFM. The force $\overrightarrow{\mathcal{F}}$ is exerted on a surface determined by the zero-flux interatomic surfaces separating the atoms in the tip from those in the sample, and thus its response is a consequence of the atomic form of matter.[27]

The definition of pressure requires the existence of a surface upon which the pressure is exerted placing it within the realm of the physics of an open system. A scaling procedure demonstrates that the expectation value of the pressure−volume product of a proper open system is proportional to its surface virial, the virial of the Ehrenfest force exerted on its surface.[28] 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 force $\overrightarrow{\mathcal{F}}$ 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 its confining walls as opposed to previous treatments based on the analogy with the classical virial theorem for a contained gas wherein the pressure−volume product was incorrectly related to the virial of the "wall forces".

These examples demonstrate that the Ehrenfest force is the one acting on and between macroscopic systems, controlling in addition their relative motion. It is thus the one that determines the force required to separate two surfaces and the study of the adhesive properties of surfaces should be directed toward an understanding and prediction of the Ehrenfest force that is established when two surfaces are brought into contact.

Energy Changes

The virial theorem plays a central role in defining the energy of an open system.[4,5] Its statement for an open system is of the same form as that given in eq 2 for the Ehrenfest force: in this case the time rate of change of $\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}$ is equated to the expectation value of $(i/\hbar)[\hat{H}, \hat{\mathbf{r}}\cdot\hat{\mathbf{p}}]$ plus a surface term $\mathcal{V}_s(A)$, denoting the flux in the associated current density that is expressible as $\mathbf{r}\cdot\sigma(\mathbf{r})$. The expectation value of the commutator yields $2T(A) + \mathcal{V}_b(A)$, twice the electronic kinetic energy T plus the virial of the Ehrenfest force exerted over the basin of the atom. For a stationary state the atomic statement of the virial theorem yields $2T(A) + \mathcal{V}_b(A) +$

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$\mathcal{V}_s(A) = 0$. Expressing by $\mathcal{V}(A)$ the total virial for an open system A, $\mathcal{V}(A) = \mathcal{V}_b(A) + \mathcal{V}_s(A)$, the virial theorem for a stationary state may be stated as

$$-2T(A) = \mathcal{V}(A) = \mathcal{V}'_b(A) + \mathcal{V}'_s(A) \qquad (7)$$

The virials of the Ehrenfest force exerted over the basin and the surface of the atom with the origin for the coordinate **r** placed at the nucleus of atom A are given in eq 8

$$\mathcal{V}'_b(A) = -\int_A \mathbf{r}_A \cdot \vec{\mathcal{A}}(\mathbf{r})d\mathbf{r} = -\int_A \mathbf{r}_A \cdot \nabla \cdot \vec{\sigma}(\mathbf{r})d\mathbf{r}_s(A)$$

$$\mathcal{V}'_s(A) = \oint dS(A, \mathbf{r}_s)\mathbf{r}_A \cdot \vec{\sigma}(\mathbf{r}) \cdot \mathbf{n}_A(\mathbf{r}) \qquad (8)$$

An alternative expression for $\mathcal{V}'_b(A)$ in a stationary state in terms of the stress tensor is also given in eq 8. One notes that $\mathcal{V}'_b(A)$ is the virial of the Ehrenfest force acting over the basin of the atom and $\mathcal{V}'_s(A)$ is the virial of the Ehrenfest force acting on its surface. The current in the surface virial has the dimensions of F/L or surface tension, and $\mathcal{V}'_s(A)$ is thus a measure of the surface energy associated with the interaction of A with its bonded neighbors.

We shall be concerned with molecules in equilibrium geometries wherein no forces act on the nuclei and $\sum_A \mathcal{V}(A) = V$, the total potential energy of the molecule. Under these conditions, one may employ the virial theorem to relate the change in the total energy to the changes in the kinetic energy T and the potential energy V with no contributions from the virials of external forces. Thus $\Delta E = -\Delta T = {}^1/_2 \Delta V$ where Δ denotes the difference between any two states of the system for which the forces on the nuclei vanish. The change in energy for some total system, ΔE, may be expressed in terms of the changes in the potential energy contributions of the individual atoms in one of two ways. First, one may equate the change ΔV to the sum of the changes in the electron−nuclear attractive energies ΔV_{en} plus a term ΔV_r grouping the two repulsive contributions from the electron−electron and nuclear−nuclear terms, as done in eq 9

$$\Delta E = {}^1/_2 \sum_A \{\Delta V_{ne}(A) + \Delta V_{ee}(A) + \Delta V_{nn}(A)\} =$$
$${}^1/_2 \sum_A \{\Delta V_{ne}(A) + \Delta V_r(A)\} \quad (9)$$

Alternatively, one may equate ΔE to the changes in the basin and surface virials

$$\Delta E = {}^1/_2 \sum_A \Delta \mathcal{V}(A) = {}^1/_2 \sum_A \{\Delta \mathcal{V}_b(A) + \Delta \mathcal{V}'_s(A)\} \quad (10)$$

Equation 10 divides $\Delta E(A)$ into two contributions: one from the change in the virial of the forces acting over the basin of the atom (with $\mathcal{V}_b(A) = \mathcal{V}(A) = V(A)$ for an isolated atom) and another from the formation of its interatomic surface (with $\Delta \mathcal{V}_s(A) = \mathcal{V}_s(A)$ for a change referenced to an isolated atom). The energy decomposition given in eq 9 is discussed first for the cage complexes.

Changes in Atomic Energies for Formation of Endohedral Cages

The electron−nuclear potential energy for atom A, the quantity $V_{en}(A)$, is given by the sum of two contributions:

the term $V_{en}°(A)$, the interaction of the electron density in the basin of atom A (the density internal to A) with its own nucleus together with the term $V_{en}^e(A)$, the interaction of the same density with all the nuclei external to A. $V_{en}^e(A)$ *yields the stabilizing interaction of the density of atom A with the nuclei of all the atoms that, together with A, are brought together in the formation of the molecule.* Thus $V_{en}^e(A)$, which is zero for an isolated atom, is necessarily negative, and it is the contributions of all the atoms to the decrease in V_{en}^e that dominates the energy of molecular formation.

$Be^{2+}@C_{10}H_{16}$. The changes in the atomic populations $N(A)$, atomic volumes $v(A)$, and total energies $E(A)$ are listed in Table 4 for the formation of each complex from separated adamantane and X. Also listed are the changes in the potential energy in terms of their attractive internal $\Delta V_{en}°(A)$ and external $\Delta V_{en}^e(A)$, and repulsive $\Delta V_r(A)$ contributions. The volume change $\Delta v(X)$ is with respect to the volume of a free X atom or ion determined by its 0.001 au density envelope, the van der Waals envelope.[29] The changes for the atoms of adamantane are for volumes determined by the intersection of their interatomic surfaces with the 0.001 au density envelope that bounds their nonbonded regions.

The principal contribution to the exothermic bonding energy of 223 kcal/mol in $Be^{2+}@C_{10}H_{16}$ is from the Be atom, with additional stabilizing changes from the C1 and C2 atoms, all of which are the recipients of electronic charge. Both the internal and external contributions to the potential energy of the carbons decrease and are sufficient to overcome the increase in the repulsive energy and lead to overall stabilization of the atoms. The hydrogens lose electronic charge, their volumes decrease, and their energies increase, contributing +652 kcal/mol to the total energy change, and overall, the insertion of Be^{2+} causes the energy of the adamantane cage to increase by 179 kcal/mol.

The largest single stabilizing contribution to the change in the potential energy of interaction is from the decrease in the external potential energy of the Be atom, the term $\Delta V_{en}^e(Be)$, a result of the interaction of its density with the nuclei of the atoms of the enclosing cage. This is a general result for all of the inserted X atoms. Electron density is transferred to X in each complex, $\Delta N(X)$ ranging from 0.28e for Be to 0.11e for Ne. Hence the internal contribution $\Delta V_{ne}°(X)$ is stabilizing but of much smaller magnitude than $|\Delta V_{en}^e(X)|$, and the bonding of the X atom is primarily the result of the stabilization of its density with the nuclei of the surrounding cage. The attractive interactions are sufficient to overcome the increase in the repulsive contributions to the energy of X in all four complexes. The bonding of X in the endohedral cage complexes is similar to that found in the transition metal carbonyls and metallocenes such as ferrocene, where the principal source of the bonding is from dominant and exceptional decrease in the energy of interaction of the atomic density on the transition metal atom with the nuclei of the surrounding ligand atoms, the contribution from the term $\Delta V_{ne}^e(M)$.[11]

$Li^+@C_{10}H_{16}$. As with the Be complex, the dominant contribution to the energy of formation of the complex is from the decrease in energy of Li and this primarily from the interaction of its density with the nuclei of the cage, the

Table 4. Changes in the Atomic Properties of X@adam from Adamantane and X[a]

A	$\Delta N(A)$	$\Delta \nu(A)$	$\Delta E(A)$	$\Delta V_{ne}°(A)$	$\Delta V_{ne}^e(A)$	$\Delta V_r(A)$
X = Be²⁺	0.2824	−6.56	−401.95	−1.4823	−48.5204	48.7215
C1	0.3311	8.54	−89.08	−0.9646	−9.0994	9.7804
C2	0.1451	5.95	−19.35	−0.3684	−5.2714	5.5785
H1	−0.2057	−11.14	57.48	0.1852	2.6228	−2.6248
H2	−0.1378	−8.28	35.11	0.1163	1.4954	−1.4997
X = Li⁺	0.1953	−14.36	−260.26	−0.8064	−46.8285	46.8052
C1	0.1424	5.98	−10.27	−0.3212	−3.7599	4.0485
C2	0.0839	4.42	8.71	−0.1526	−2.9247	3.1051
H1	−0.1076	−6.29	28.47	0.0907	1.3433	−1.3433
H2	−0.0699	−4.25	17.09	0.0568	0.6927	−0.6951
X = He	0.1011	−48.60	−327.77	−0.6362	−45.1671	44.7584
C1	−0.0188	2.63	57.26	0.2816	0.2700	−0.3690
C2	0.0105	2.94	33.61	0.1125	−0.5264	0.5211
H1	−0.0035	0.65	4.06	0.0070	0.0311	−0.0250
H2	−0.0064	0.19	3.02	0.0077	0.0011	0.0009
X = Ne	0.1095	−76.22	−903.45	−3.4059	−201.2768	201.8030
C1	−0.0055	11.83	149.55	0.6652	−6.6310	6.4428
C2	0.0311	9.85	94.09	0.3349	−7.5827	7.5480
H1	−0.0118	2.09	9.79	0.0206	−0.5856	0.5963
H2	−0.0185	1.10	8.04	0.0215	−0.7195	0.7237
X = B³⁺	0.7881	2.69	−1014.74	−4.6331	−59.3031	60.7019
C1	0.5537	10.32	−186.31	−1.6891	−16.1303	17.2260
C2	0.1149	6.83	−15.46	−0.2784	−5.8874	6.1169
H1	−0.3003	−15.32	88.95	0.2876	3.8547	−3.8588
H2	−0.2075	−11.63	56.04	0.1835	2.3680	−2.3728
X = Al³⁺	0.4681	−12.57	−1151.25	−6.4149	−207.7750	210.5206
C1	0.4126	18.20	−44.74	−0.9032	−20.6561	21.4171
C2	0.2508	13.96	−1.74	−0.4965	−16.2341	16.7254
H1	−0.2893	−14.53	86.34	0.2725	3.1363	−3.1335
H2	−0.2056	−10.87	56.48	0.1828	1.5751	−1.5778

[a] $\Delta E(A)$ in kcal/mol, $\Delta \nu(A)$ and $\Delta V(A)$ in au.

term $\Delta V_{ne}^e(Li)$. Each carbon bonded to Li is stabilized by 10 kcal/mol in forming the complex, while each methylene carbon is destabilized by 9 kcal/mol. The loss of electronic charge from the hydrogens is one-half that transferred in the Be complex as is the associated increase in their energy equal to +319 kcal/mol. The adamantane cage is destabilized by 330 kcal/mol, an increase of 151 kcal/mol over Be²⁺@C₁₀H₁₆ and overall the energy of formation of Li⁺@C₁₀H₁₆ is endothermic by 70 kcal/mol.

He@C₁₀H₁₆. The energy of formation of this complex is endothermic by 156 kcal/mol. The dominant stabilizing contribution to the energy of formation is from the interaction of the density of the He atom with the nuclei of the cage, the term $V_{ne}^e(He)$, whose magnitude outstrips the increase in the repulsive contribution, $\Delta V_r(He)$, to the atomic energy change. One notes that the value of $\Delta V_r(He)$ is less than $\Delta V_r(Be)$, He undergoing a smaller increase in its repulsive interactions with the cage than Be. The transfer of electronic charge to X is least for He, and correspondingly it undergoes the smallest of the stabilizations caused by decreases in internal energy, the quantity $\Delta V_{ne}°(He)$. The energies of both the methine and methylene carbons increase, the former losing a small amount of electronic charge the latter gaining a still lesser amount.

The potential energy contributions to the energy changes for a methine carbon C1 bonded to He are of most interest. The interaction results in a *decrease* in the repulsive energy

of C1, but its energy undergoes a net increase as a result of the decrease in magnitude of its attractive contributions. The value of $\Delta V_{ne}^e(C1)$ is the only one such contribution greater than zero for all of the complexes, and this is a result of the smaller nuclear charge on He compared to the other X atoms, in particular that for Ne with $Z = 10$, where $\Delta V_{ne}^e(C1) = −6.6$ au. The increase in the repulsive energies of the C2 atoms, $\Delta V_r(C2)$, is also less than for the insertion of Be²⁺ and the sum of the increases in repulsive energies for C1 and C2 in He@C₁₀H₁₆ is 70.9 au smaller than the corresponding sum for Be²⁺@C₁₀H₁₆. This observation coupled with the decrease in the value of $\Delta V_r(He)$ compared to $\Delta V_r(Be)$ demonstrates that the claim that the endothermicity of He@C₁₀H₁₆ is a result of 'antibonding' of He with the methine carbons of the adamantane cage has no basis in physics.[26]

The energy of the carbon framework does increase, but not because of increased repulsions with the caged atom, but rather because of destabilizations in their mutual interactions. The small loss of electronic charge from the C1 atoms and the reorganization of their densities causes the internal contributions to their potential energies, together with those for the C2 atoms, to increase and overall the energies of the carbons increase by 431 kcal/mol. The small loss of density from the H atoms causes their energy to increase by 53 kcal/mol, and the adamantane cage is destabilized by 484 kcal/mol, an increase of 305 kcal/mol over Be²⁺@C₁₀H₁₆.

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Thus the endothermicity of He@$C_{10}H_{16}$ compared to the exothermicity of Be^{2+}@$C_{10}H_{16}$ is not a result of a repulsion between the X atom and the surrounding cage, a quantity that is actually less for He than for Be^{2+}, but because of the *decrease* in the attractive contributions to the energies of the carbons of the cage.

Ne@$C_{10}H_{16}$. The Ne complex has an endothermicity of 395 kcal/mol. The single largest change in the atomic energies for the Ne atom, as for the X atom in the other complexes, is a result of the stabilizing decrease in the energy of interaction of the density of the Ne atom with the nuclei of the cage. The endothermic energy of formation is again a result of the destabilization of the cage, and primarily from the increase in energy of the carbon atoms, the methine carbons in particular, whose energies increase by 1164 kcal/mol. Unlike the He complex where the repulsive energies of the methine carbons actually decrease on bonding, both sets of carbons in the Ne complex have positive $\Delta V_r(C)$ values that are only slightly less than the magnitude of the decreases in the values of $\Delta V_{en}^e(C)$. The internal contributions $\Delta V_{en}°(C)$ are also positive, and the carbons are destabilized in their interactions with the Ne atom. The discussion of the data for $B^{3+}C_{10}H_{16}$ is reserved for the demonstration of the dominant role in the stabilization of the complexes played by the charge transfer from the hydrogens to the cage interior.

Bonding as Viewed through the Changes in the Basin and Surface Virials. While the virial $\mathscr{V}(A)$ is independent of the choice of origin, its expression in terms of basin and surface contributions is not. However by placing the origin at the position of the nucleus, as done in eq 8, one can obtain a unique expression for the potential energy change as a sum of basin contributions and interatomic surface terms, the latter depending only upon the internuclear separation between the bonded nuclei. The surface terms determine the contribution to the potential energy of interaction stemming from the formation of each surface A|B. Just as the Ehrenfest force on the surface of A can be equated to a sum of contributions, one from each of the interatomic surfaces bounding A, eq 6, so $\mathscr{V}_s(A)$ can be similarly expressed, with the contribution from a bonded neighbor B denoted by $\mathscr{V}_s(A|B)$. Summing the contributions to the energy of the surface $S(A|B)$ between A and B and defining $\mathbf{R}_{ab} = \mathbf{r}_a - \mathbf{r}_b$, the vector from the nucleus of B to that of A, and noting that $\mathbf{n}_A = -\mathbf{n}_B$, one obtains[4]

$$V_s(A||B) = \mathscr{V}_s'(A|B) + \mathscr{V}_s'(B|A) =$$
$$\mathbf{R}_{ab} \cdot \oint dS(A|B;\mathbf{r}_s)\vec{\sigma}(\mathbf{r}) \cdot \mathbf{n}_A(\mathbf{r}) = \mathbf{R}_{ab} \cdot \vec{\mathscr{F}}(A|B) \quad (11)$$

This expression equates the sum of the surface virials from two atoms sharing a common surface $S(A|B)$ to the scalar product of the Ehrenfest force acting on the surface with the vector $\mathbf{R}_{ab}$, and the dependence of the two surface integrals on individual origins is replaced by the physical separation between the nuclei of the bonded atoms. Thus the energy of formation of a molecule from separated atoms can be expressed in terms of contributions from the changes in the potential energy within each atomic basin plus a contribution from the virial of the Ehrenfest force $\vec{\mathscr{F}}(A|B)$

acting on the interatomic surface between each pair of bonded atoms denoted by $\mathscr{V}_s(A||B)$, eq 12

$$\Delta E = \frac{1}{2}\sum_A \mathscr{V}_b'(A) + \frac{1}{2}\sum_{A|B} \mathscr{V}_s'(A||B) \quad (12)$$

The Ehrenfest force $\vec{\mathscr{F}}(A|B)$ is attractive when the force exerted on the density of atom A is directed at B, the situation found for all of the bonded interactions in the cage complexes. The combined surface virial $\mathscr{V}_s(A||B)$ is negative in such a case, and the formation of the interatomic surface $S(A|B)$ contributes to the stability of the system.

The data for the implementation of eq 12 are given in Table 5 which also lists the separate values of $\Delta \mathscr{V}_s(A)$. The changes in both the basin and surface virials are stabilizing for the X atom in all four complexes, with the magnitude of $\Delta \mathscr{V}_s(X)$ increasing in the order Be → Ne. The basin virials for the carbons are destabilized by relatively small amounts in the Be and Li complexes, and their net stabilization is a result of the changes in their surface virials. The carbons in the He and Ne complexes undergo destabilizing increases in both their basin and surface virials, as do the hydrogen atoms in all four complexes.

The energies of the surface virials are given in kcal/mol to better gauge their relative contribution to energies of formation of the complexes. The energy of the X|C1 surface, as determined by the $\frac{1}{2}\mathscr{V}_s(X||C1)$, is stabilizing in every complex, ranging from −112 kcal/mol in Be^{2+}@$C_{10}H_{16}$ to −247 kcal/mol in Ne@$C_{10}H_{16}$. The energy of the C1|C2 surface decreases slightly in the formation of Be^{2+}@$C_{10}H_{16}$ but increases in the remaining complexes, as do the energies of the C1|H1 and C2|H2 surfaces. In summary, the Ehrenfest force, which is attractive for all of the bonded interactions in these molecules, decreases in magnitude for all of the interactions within the adamantane cage with the exception of the C1|C2 surface in Be^{2+}@$C_{10}H_{16}$. Thus the adamantane cage is destabilized in the formation of the complexes by the destabilization of the basin virials of both the C and H atoms and by increases in the energies of the surface integrals internal to the cage, the latter resulting in a decrease in the stability of their bonded interactions. Contrawise, the energy of formation of the atomic surface bounding the X atom is stabilizing in every case, as is the energy of formation of the X|C1 surface, and these interactions contribute to the stabilization of the complexes.

Discussion and Conclusions

The role of the Ehrenfest force in the physics of an open system brings to the fore the unifying understanding provided by the virial theorem. Slater refers to Feynman's electrostatic theorem and the virial theorem as 'two of the most powerful theorems applicable to molecules and solids'.[30] To this one should add the Ehrenfest force, since it is the virial of this force that determines the electronic virial in Slater's molecular theorem.[20] The Ehrenfest force includes the electrostatic force of attraction of the density by the nuclei but not the nuclear repulsion. Consequently, the nuclear contribution to $\mathscr{F}$ equals the difference between the net Feynman force acting on the nuclei and the nuclear repulsive forces, thereby

Table 5. Changes in Atomic Basin and Surface Virials and with Surface Virials for Individual Bonded Interactions[a]

A	$\Delta\mathcal{V}_b(A)$ au	$\Delta\mathcal{V}_s(A)$ au	$\mathcal{V}_s$ (X‖C1) kcal/mol	$\Delta\mathcal{V}_s$ (C1‖C2) kcal/mol	$\Delta\mathcal{V}_s$ (C1‖H1) kcal/mol	$\Delta\mathcal{V}_s$ (C2‖H2) kcal/mol
X = Be^{2+}	−0.6824	−0.5983	−223.52	−38.72	32.13	17.95
C1	0.0337	−0.3196				
C2	0.0236	−0.0872				
H1	0.1177	0.0655				
H2	0.0695	0.0425				
X = Li$^+$	−0.1609	−0.6682	−212.35	22.72	17.32	9.41
C1	0.0461	−0.0791				
C2	0.0423	−0.0155				
H1	0.0515	0.0392				
H2	0.0312	0.0232				
X = He	−0.0268	−1.0177	−282.63	55.53	3.20	2.82
C1	0.1656	0.0167				
C2	0.0842	0.0222				
H1	0.0018	0.0112				
H2	0.0032	0.0065				
X = Ne	−0.8497	−2.0274	−494.42	124.06	8.85	7.22
C1	0.3418	0.1339				
C2	0.1961	0.1007				
H1	0.0069	0.0242				
H2	0.0092	0.0164				

[a] For adamantine, $\mathcal{V}_s$(C1‖C2) = −0.3174; $\mathcal{V}_s$(C1‖H1) = −0.1318; $\mathcal{V}_s$(C2‖H2) = −0.1314.

accounting for the appearance of V_{nn} and the virial of the Feynman forces in the virial of the forces exerted on the electrons.[4]

The use of these theorems provides answers to the questions raised in the Introduction concerning the possible presence of repulsive interactions between X and the carbons of the cage[26] and of the storage of the excess energy in the endothermic complexes. The Ehrenfest force in a stationary state is balanced locally by the divergence of the stress tensor, $\vec{\mathcal{F}}(\mathbf{r}) + \nabla\cdot\vec{\sigma}(\mathbf{r}) = 0$, as its integrated value $\vec{\mathcal{F}}(A)$ is by the surface integral of $\vec{\sigma}(\mathbf{r})$, eq 6. However, as discussed in the Introduction, $\vec{\mathcal{F}}(A)$ enables one to determine the force acting over the basin of an atom and to determine how this force is balanced on the surface it shares with each of its neighbors. This is new information regarding the mechanics of bonding between atoms, information that underlies the accompanying energy changes because it is the virial of the Ehrenfest force that determines the potential energy changes. It is the nature of this force, that within the regime of equilibrium geometries, it is always found to be attractive, drawing each atom toward its neighbor such that the resultant force on the atom is zero. Thus one may extend the definition of bonding between atoms denoted by a bond path: *the presence of a line of maximum density linking a pair of nuclei in an equilibrium geometry of a bound state or one lying within the attractive region of a potential well—atoms linked by a bond path—implies not only the absence of repulsive Feynman forces on the nuclei but also the presence of attractive Ehrenfest forces acting across the interatomic surface shared by the bonded atoms.* This observation underlies the mirroring of a bond path by a virial path, a line of maximally stabilizing potential energy density.[10] This definition certainly applies in the case of the endohedral complexes, where the Ehrenfest force $\vec{\mathcal{F}}(X|C1)$ acting across each X|C1 surface is attractive and the interactions

denoted by the corresponding bond paths are a consequence of attractive forces acting between the X and C1 atoms.

Since the force $\vec{\mathcal{F}}(X|C1)$ is attractive, the derived surface virial $\mathcal{V}_s(X‖C1)$, eq 11, a quantity that determines the contribution to the energy change resulting from the formation of the surface X|C1, is stabilizing. While $\mathcal{V}_s(A‖B)$ is not a bond energy for A|B—a quantity not defined within the physics of an open system—its change during the formation of the complex provides a quantitative gauge of the distribution of the energy increase over the bonded interactions caused by an endothermic insertion of X. The values of $\mathcal{V}_s(A‖B)$, Table 5, demonstrate that the energy increases incurred by the insertion of Li$^+$, He, and Ne are mirrored solely in the surface virials of the atoms comprising the adamantane cage, the formation of the X|C1 surfaces yielding stabilizing contributions in all cases. These changes are reflected in the energy changes for the individual atoms, Table 4, with only the energies of X and of C1 in Li$^+$@C$_6$H$_{10}$ contributing to the lowering of the energy of formation in the endothermic reactions.

The principal factor contributing to the stabilization of an endohedral complex may be determined by a comparison of the atomic properties for the formation of exothermic Be^{2+}@C$_{10}$H$_{16}$ with the endothermicity of the remaining complexes. The exothermicity has its origin in the transfer of charge from the hydrogens to the interior of the cage, to the carbons, and to the positively charged Be atom, rather than being a consequence of the smaller volume of the Be atom. The similar but much smaller flow of density from the hydrogens to the interior of the cage caused by the smaller positive charge on Li is insufficient to overcome the attendant destabilization resulting form the larger volume of Li. If the charge transfer to the cage interior is indeed paramount in leading to stabilization of the insertion complex, one would predict an even larger exothermicity for the insertion of a

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B^{3+} ion and this is indeed the case. The formation of $B^{3+}@C_{10}H_{16}$ is predicted to be exothermic by 826 kcal/mol compared to an exothermicity of 223 kcal/mol for $Be^{2+}@C_{10}H_{16}$. There is a transfer of 3.7e from the hydrogens to the cage interior in $B^{3+}@C_{10}H_{16}$ compared to 2.5e in $Be^{2+}@C_{10}H_{16}$, with 0.79e being transferred to B, Table 4. While the volume of a free B^{3+} ion is less than that of free Be^{2+}, the volume of the boron atom in the complex is actually greater than that for Be, 9.6 compared to 7.2 au, a consequence of a greater transfer of electronic charge to the boron atom. The data in Table 4 show that the pattern of changes in the atomic energies for the formation of the boron complex mimic those for the Be complex, but all are of greater magnitude. One notes in particular the increase in the magnitude of the internal potential energy change for B compared to Be, all increases being a consequence of the flow of density from the hydrogens to the cage interior. The same increase in exothermicity of formation with increase of positive charge on X is found for $Al^{3+}@C_{10}H_{16}$ for which ΔE is predicted to equal -318 kcal/mol, a consequence of a transfer of 3.6e of electronic charges from the hydrogens to the interior of the cage. This increase in the stability of $Al^{3+}@C_{10}H_{16}$ compared to $Be^{2+}@C_{10}H_{16}$ is obtained despite the volume of the Al atom in the complex being greater than that for the Be atom, $v(Al) = 17.3$ au compared to $v(Be) = 7.2$ au and in spite it exhibiting the largest increase in the C1–C2 separation, equal to 0.39 au.

The theory of atoms in molecules provides a comprehensive understanding of the relative stabilities of endohedral complexes and of the mechanism of energy storage within the complex, all in terms of the atomic expectation values for populations, energies and forces obtained from the physics of an open system.

Haaland et al.[26] in a critique of the statement that the presence of a bond path linking two atoms implies that the atoms are bonded to one another state "Most chemists would probably agree that the defining property of a chemical bond is the existence of a positive bond rupture energy, that is, the energy of the molecule is lower than the energy of the fragments,...". This is followed by the division of the endothermicity for the formation of $He@C_{10}H_{16}$ by four to account for the presence of the four bond paths linking He to the methine carbons, to give "a negative He–C mean bond energy of -39 kcal/mol". In their words "the interaction is *antibonding*". There is no explanation of the force responsible for this 'antibonding', occurring as it does in the absence of Feynman forces on the nuclei and wherein the Ehrenfest forces between the bonded atoms are attractive.

The response to this criticism requires that one correct for a number of misunderstandings of the theory by the authors. First, concerning the question posed in the title to their paper "Is the presence of an atomic interaction line in an equilibrium geometry sufficient condition for the existence of a bond?" and their reference to 'a chemical bond' in rationalizing the definition of a bond energy; there is no attempt to define a 'bond' in QTAIM since a bond has no definable nor identifiable physical form. Rather theory accounts for 'bonding between atoms', the presence of a bond path denoting that the atoms so linked are 'bonded to one another'.

All of the properties that are traditionally associated with the presence of a 'bond' such as 'bond energy' or 'bond length' are, in fact, consequences of the occurrence of 'bonding between atoms'. As illustrated in this paper, one may bring all of quantum mechanics to bear on the forces and energetics of bonding using the physics of an open system. There is no unique, unambiguous definition of a 'bond energy' in a polyatomic molecule in traditional chemistry. The authors raise anew previous claims of bond paths being present in cases where the interactions are 'clearly repulsive',[31,32] claims that have been previously dealt with.[8,33,34]

Their conclusion that the X|C1 interaction is 'antibonding' is at variance with the observation that the Ehrenfest force $\vec{\mathcal{F}}(X|C1)$ is attractive and that the formation of the X|C1 surface makes a stabilizing contribution to the energy of formation, with $\mathcal{V}_s(X||C1) < 0$. The destabilizing contributions to the total energies of insertion of X are confined to the interactions between the atoms of the adamantane cage, as evidenced by the changes in their atomic energies and the basin and surface virials. Indeed, as noted above, the repulsive contribution ΔV_r to the atomic energy changes for X and the carbon atoms are less for endothermic $He@C_{10}H_{16}$ than for exothermic $Be^{2+}@C_{10}H_{16}$. The argument given by Haaland et al. to rationalize the stabilizing decrease in the energy of the He atom upon insertion with its 'antibonding' character avoids all appeal to quantum mechanics and the forces operative in a molecular system and instead ascribes it to the 'density of the He dropping abruptly to zero at its four interatomic surfaces', a statement displaying a complete lack of understanding of the physics of an open system and its theorems. The stabilization of the X atoms in the complexes is a result of simple physics; of the attractive interaction of the density of X with the nuclei of the atoms in the adamantane cage, the values of $V_{en}^e(X)$ given in Table 4. While arbitrary models cannot be used to criticize conclusions that are obtained from physics, one may employ QTAIM in a complementary manner to determine viability of orbital models—the recovery of the Dewar-Chatt-Duncanson $d\pi$-$p\pi^*$ model[35,36] of back-bonding in terms of the quadrupole polarizations of the ligand atoms being a recent example.[11,37]

If one generalizes the argument of Haaland et al., then one must postulate the presence of undefined 'antibonding interactions' in all stable configurations other than the one of lowest energy. A molecule at thermal equilibrium in a stationary state has no memory of how it attained that state, from one of higher or lower energy. To postulate the presence of unknown repulsive forces in a molecule in an equilibrium geometry based on an anthropomorphic bias contributes nothing to the physical understanding of bonding.

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(34) The bond paths found between Cl atoms in substituted cyclohexanes and judged by Cioslowski et al.[31] to be repulsive are similar in all respects to those linking neighboring atoms in solid molecular chlorine, interactions that account for its layered structure. If these interactions were repulsive, solid chlorine would not exist. Those who doubt the universal identification of a bond path with bonding by citing the presence of bond paths between anions in an ionic crystal[32] should differentiate between classical models of bonding and its proper quantum mechanical description.[8] The description of an ionic crystal as one whose cohesive energy is determined by electrostatic forces between the ions together with short-range core repulsions is a classical model without foundation in quantum mechanics. Matter is a distribution of charge in real space−of pointlike nuclei embedded in the diffuse density of electronic charge, $\rho(\mathbf{r})$, defined as the expectation value of the density operator. The properties of $\rho(\mathbf{r})$ are determined by the local statements of the theorems of quantum mechanics, the most important being the Ehrenfest force theorem, determining its equation of motion, and the virial theorem, governing its energy. There is nothing in the quantum description of the energy corresponding to the classical model of interacting ions. In particular there are no resultant Ehrenfest forces acting on the atoms and no net forces, neither attractive nor repulsive, acting on the atomic nuclei, since the Feynman forces are zero and any displacement of a nucleus results in the creation of a force restoring it and its associated density to its equilibrium position. The model is useful for pedagogical purposes, but it should not be used to criticize the quantum mechanical description of bonding.

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