Universal Parameter Tight-Binding Molecular Dynamics: Application to C_{60}

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First-principles molecular-dynamics simulation is carried out for covalent systems with arbitrary (i.e., tetrahedral and nontetrahedral) coordination in a nonorthogonal, tight-binding basis, generalizing previous successful applications to tetrahedral solids. The generalized method is applied to study various aspects of the C_{60} molecule, including the effect of doping on vibrational modes, and interaction with heteroatoms. Considerable increase in the double-bond length and a much smaller increase in the single-bond length are found. Oxygen chemisorption occurs over the bridge site along the carbon-carbon double bond, weakening the latter.

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The interest in first-principles molecular dynamics (or Born-Oppenheimer dynamics), i.e., simulations in which the interaction between atomic centers is not determined from model potentials, has increased significantly since the pioneering work of Car and Parrinello [1]. Their work was an *ab initio* calculation in which the forces were determined from electronic energies calculated in the local-density approximation. A first-principles molecular-dynamics method to deal with questions of chemisorption on semiconductor surfaces, based on Harrison's universal parameter tight-binding method [2], was developed by Menon and Allen [3] at about the same time as the *ab initio* developments. These authors used an effective subspace Hamiltonian technique [4] to reduce the size of the simulated system, while fully including the effect of the electronic structure of the remaining atoms in the entire substrate exactly with a Green's-function approach. With many additional novel computational techniques [5], Menon and Allen were able to investigate successfully such complex questions as the initial breakup of molecules at GaAs surfaces during chemical vapor deposition [6].

More recently, Wang, Chan, and Ho [7,8] have applied a first-principles tight-binding molecular-dynamics method to study defects in tetrahedral solids using large clusters, and found excellent results. They also used Harrison's universal parameter tight-binding method in the electronic energy calculations, as in the chemisorption studies of Menon and Allen, although they did not use a bulk Green's function to avoid doing a large cluster calculation. Khan and Broughton [9], Sankey and Niklewski [10], and Laasonen and Nieminen [11], have also used the tight-binding molecular-dynamics method to study tetrahedral systems.

There are some basic limitations in the above formulations. First, the method is not applicable as it stands for coordination that is not tetrahedral. This is because Harrison's original formulation [12] explicitly assumed orthogonal tetrahedral hybrid orbitals. Single two-center bonds dominate the electronic structure for tetrahedrally coordinated compounds and the nonorthogonality between atomic orbitals, responsible for repulsion in the bond, can be separated out as a simple two-body repulsion. For more general coordination, however, the nonorthogonality cannot be so isolated and it becomes necessary to resort to matrix elements of nonorthogonal atomic orbitals [13]. Thus, even the inclusion of next-nearest-neighbor effects requires modifications of the standard formulation. In this Letter, we generalize the molecular-dynamics formulation so as to apply for nontetrahedral systems as well. Our work is based on a corresponding generalization for electronic energy calculations made by van Schilfgaarde and Harrison [13,14]. This allows this universal parameter theory to be applicable (within the usual limits of a one-electron theory) to study the molecular dynamics of molecules, crystals, defects, and surfaces in a computationally tractable way. This particular formulation, while equivalent in spirit to the extended Hückel method popular among chemists [15,16], lends itself to first-principles molecular dynamics with significant reduction in computational effort. As an illustration, we have studied some aspects of C_{60}, a molecule of great current interest. In particular, we have examined the effect of doping on the vibrational modes, and the interaction of C_{60} with oxygen atoms.

We begin with a brief presentation of the molecular-dynamics formulation. More details will be published elsewhere. Our formulation is based on van Schilfgaarde and Harrison's nonorthogonal-orbital tight-binding electronic structure calculation [13]. The molecular-dynamics formulation proceeds in a manner similar to the tetrahedral case [3]. If the total energy U of a system is known, the force F_x associated with an atomic coordinate x is given by

$$F_x = -\frac{\partial U}{\partial x}\,. \tag{1}$$

One can then easily do molecular-dynamics simulations by numerically solving Newton's equation

$$m\frac{d^2x}{dt^2} = F_x \tag{2}$$

to obtain x as a function of time. We write U as a sum of two terms [5],

$$U = U_{\mathrm{el}} + U_{\mathrm{rep}}\,, \tag{3}$$

where $U_{\rm el}$ is the sum of the one-electron energies E_k,

$$U_{\rm el}=\sum_k^{\rm occ} E_k \, , \tag{4}$$

and $U_{\rm rep}$ is given by a repulsive pair potential $\phi(r)$,

$$U_{\rm rep}=\sum_i \sum_{j(>i)} \phi(r_{ij}) \, . \tag{5}$$

Here r_{ij} is the separation of atoms i and j, and $\phi(r)$ is taken to scale exponentially with distance [3]. Note that for tetrahedral systems with orthogonal, hybrid orbitals with nearest-neighbor overlap, the separation into a pairwise repulsive part is exact [2], but not for the general case [12]. The electronic part of the force is given by [3]

$$F_x^{\rm el}=\sum_k^{\rm occ} \frac{\partial F_k}{\partial x} \, . \tag{6}$$

The evaluation of the force is described next. The eigenvalue equation for a system is given by

$$(H-E_n S)\psi_n=0 \, . \tag{7}$$

Let $\{\phi_a\}$ be a complete set of nonorthogonal atomic orbitals. Then one can write the eigenstates ψ_n of this system as a linear combination of the ϕ_a,

$$\psi_n=\sum_a c_a^n \phi_a \, . \tag{8}$$

The eigenvalue problem (7) then becomes

$$\sum_j (H_{ij}-E_n S_{ij}) c_a^n=0 \, , \tag{9}$$

where

$$H_{ij}=\int \phi_i^* H \phi_j \, d\mathbf{r} \tag{10}$$

and

$$S_{ij}=\int \phi_i^* \phi_j \, d\mathbf{r} \, . \tag{11}$$

In matrix form Eq. (9) becomes

$$(\mathbf{H}-E_n \mathbf{S})\mathbf{C}^n=0 \, , \tag{12}$$

where $\mathbf{C}^n$ is a column vector with coefficients c_i^n's.

By taking the derivative of (12) with respect to x and multiplying on the left with $\mathbf{C}^{n\dagger}$, it is easily seen that

$$\frac{\partial E_n}{\partial x}=\frac{\mathbf{C}^{n\dagger}(\partial \mathbf{H}/\partial x - E_n \, \partial \mathbf{S}/\partial x)\mathbf{C}^n}{\mathbf{C}^{n\dagger}\mathbf{S}\mathbf{C}^n} \, . \tag{13}$$

The electronic part of the total force can now be obtained from the above expression.

The additional complication of calculating the overlap matrix was dealt with by Harrison [12] in the spirit of extended Hückel theory [15], assuming a proportionality between **S** and **H**:

$$S_{ll'm}=\frac{2V_{ll'm}}{K(\varepsilon_l+\varepsilon_{l'})} \, . \tag{14}$$

While in extended Hückel theory **S** is explicitly calculated assuming Slater-type atomic orbitals and **H** from the above proportionality, in Harrison's approach **H** is computed from the universal parameters ($V_{ll'm}$) used successfully for tetrahedral compounds with **S** computed from the assumed proportionality. The only additional parameter is the Hückel proportionality constant K, which fixes the correct equilibrium spacing. The total electronic energy has a repulsion term proportional to S_2, where

$$S_2=\frac{(S_{ss\sigma}-2\sqrt{3}S_{sp\sigma}-3S_{pp\sigma})}{4} \tag{15}$$

is the nonorthogonality between sp^3 hybrids. In tetrahedral compounds this term separates simply into an additive two-body repulsion. van Schilfgaarde and Harrison [14] used Hückel theory to obtain

$$H_{ll'm}=V_{ll'm}[1+1/K-S_2^2] \, . \tag{16}$$

Equations (14)-(16) are used to construct **S** and **H**. The eigenvalues of a system with nonorthogonal basis set, for obtaining the electronic part of the force, can then be obtained from setting

$$\det|H_{ij}-ES_{ij}|=0 \, . \tag{17}$$

As an illustration, we have applied this formulation to simulate the dynamics of the buckminsterfullerene molecule (C_{60}) [17], which has very interesting structural [18], dynamical [19], and electronic properties [20] including superconductivity in the doped solid [21,22]. We have used the values for carbon from Harrison's table of universal matrix elements [2]. The matrix elements are assumed to scale exponentially with distance, as in many other similar works [3,5]. The only other parameters to be fixed are K, the proportionality constant to evaluate **S**, and the strength of the pairwise repulsion, U_0. K is expected to be near 2 [15], and should be larger than the value for diamond taken by Harrison [12] based on bond-length considerations. We take $K=2.1$. U_0 is taken to be 0.84 eV (based on experience with semiconductors), and results are not sensitive to this parameter. We make no attempt to adjust parameters to get quantitative agreement for properties. We first obtained the equilibrium structure by starting from a nearly correct configuration and allowing all the atoms to relax by removing 1% of each velocity at each time step. This initial simulation lasted for about 1 ps. In the final equilibrium configuration for C_{60}, two distinct carbon-carbon bond lengths were obtained. These were 1.389 Å for the bonds that are part only of hexagonal rings ("double bonds") and 1.415 Å for the bonds that are shared by hexagonal and pentagonal rings ("single bonds"), in agreement with the known existence of two bond lengths [18]. It should be noted, however, that simulations using the tight-binding theory with universal matrix elements between orthogonal orbitals, including only the nearest-neighbor interactions, yielded a single carbon-carbon bond length in C_{60} for all atoms; naively extending the range of interaction while assuming orthogonality leads to a collapse of the structure, illustrating the limitations of the earlier formulations when applied to systems dominated by multicenter bonds.

Our calculated electronic energy levels are consistent with those found from other methods [23,24], which in turn agree with photoemission experiments [25]. The vibrational motion to determine frequencies can be induced by giving all these atoms an appropriate small displacement from equilibrium. In Fig. 1 we show a simulation run for a typical carbon atom in this cluster. The unit of time step for all simulations is 2.72×10^{-16} s. The unit of distance is 0.77 Å. The normal coordinate for the radial "breathing mode" (A_{1g} symmetry) is also shown in the figure. Its frequency is determined to be 682 cm^{-1}. Similarly, by examining the normal coordinate for the A_{1g} "tangential mode," we find the frequency to be 1974 cm^{-1}. Experimental frequencies for isolated fullerene molecules are not available. These frequencies are in the general range of other theoretical results [26], but somewhat higher than experimentally observed values for the solid (497 and 1469 cm^{-1}, respectively) [27]. The quantitative disagreement is not surprising given the fact that we are using universal parameters to model the interactions. One can improve the agreement by fine tuning these quantities for specific systems. In the current work, however, we are mainly concerned with the applicability of the present general formulation for various systems, C_{60} being one among them. We note in passing that the naive nearest-neighbor orthogonal-orbital treatment gives a breathing mode frequency of 1258 cm^{-1}, about a factor of 3 too large.

Using the present formulation, molecular-dynamics simulations for chemisorption of atoms belonging to various chemical species on a C_{60} cluster can be performed easily. Although these simulations are performed for periods of the order of a picosecond, valuable information can be obtained about the relative stabilities of different sites by comparing total energies obtained at the end of each simulation. We choose oxygen as an external atom for our chemisorption studies on C_{60}. The C-O chemisorption bond length in all our simulations was determined to be 1.4 Å, which is also the sum of the covalent radii of these two atoms. The total energy calculated for bonding at a carbon-carbon bridge site over a double bond (see Fig. 2) was lower than that for bonding over a single carbon atom by 0.24 eV. Chemisorption over a double bond also causes the bond between the two carbon atoms, to which the oxygen bonds, to stretch to 1.47 Å from 1.39 Å, indicating a weakening of the carbon-carbon bond. This strongly suggests that fullerene is destabilized by reaction with atomic oxygen. There is indication that the molecule is degraded in the presence of oxygen and UV light [28].

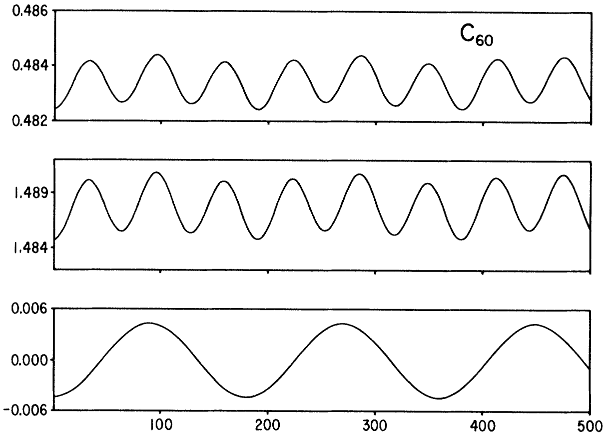

FIG. 1. The time dependence of the x coordinate (top panel) and the y coordinate (middle panel) of a typical atom in C_{60}. The initial conditions were such that the motion is dominated by the high-frequency A_{1g} mode. The bottom panel shows the time dependence of the normal coordinate for the lower-frequency A_{1g} mode. The distances are in units of 0.77 Å, and time steps are in units of 2.72×10^{-16} s.

The effect of doping can also be readily studied using the present technique within a one-electron picture. However, our treatment goes beyond the "rigid band" picture, in that molecular relaxation upon the addition of electrons is taken into account. We restrict our attention to doping with potassium. First of all, we find that the potassium 4s orbital does not hybridize with the carbon orbitals of the C_{60} molecule, but merely transfers its electron to the lowest unoccupied orbital of fullerene. Thus, we model alkali-metal doping by merely adding electrons to the host molecule. This is similar to the behavior in intercalated graphite [29]. In the neutral ground state the Fermi level falls in the gap between a completely filled fivefold degenerate state and an empty threefold degenerate state. We add an electron to this system and allow it to relax using molecular dynamics. The dependence on the dopant concentration x (in $C_{60}K_x$) of the change in the average radius of the molecule Δr, the double-bond

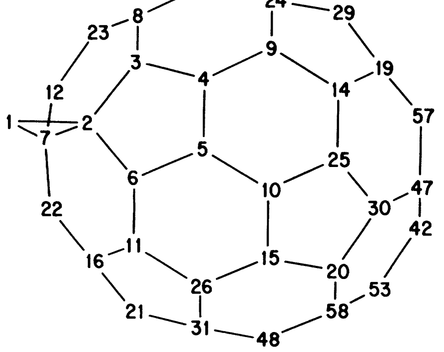

FIG. 2. The most stable equilibrium position of the oxygen atom (labeled 1) on the surface of C_{60} obtained by molecular-dynamics simulation. The carbon-carbon double bond 2-7 is weakened by oxygen chemisorption.

TABLE I. Dependence of change in average radius (Δr), change in double-bond length (Δl), radial mode frequency shift ($\Delta\omega_r$), and tangential mode frequency shift ($\Delta\omega_t$) on the dopant concentration x in $C_{60}K_x$.

x	Δr (Å)	Δl (Å)	$\Delta\omega_r$ (cm^{-1})	$\Delta\omega_t$ (cm^{-1})
0.017	0.005	0.004	−7	−49
0.033	0.007	0.007	−11	−53
0.050	0.009	0.022	−12	−63

length Δl, the radial A_{1g} mode $\Delta\omega_r$, and the tangential A_{1g} mode $\Delta\omega_t$ is shown in Table I. The average radius of the molecule increases with added electrons; this behavior is similar to that found in graphite, namely, an increase in the lattice constant with donor doping [30]. However, the dependence here is stronger than in graphite. Also, we find that the double bonds increase in length an average of 3 times more than the single bonds, with the change ranging up to 0.029 Å upon addition of three electrons. The vibrational modes also soften upon doping, again more than in graphite [29]. The softening of the tangential mode upon doping with alkali metals to saturation has been observed [31]. As pointed out by Pietronero and Strässler [30,32], the dependence of the lattice constant and frequency shift on charge transfer is related to quantities that determine the electron-phonon coupling strength. Our results suggest that the latter is stronger in fullerenes than in graphite. We are presently extending our calculations to the case of a crystal in order to derive quantitative results.

In conclusion, we have generalized the universal matrix-element tight-binding molecular dynamics to nontetrahedral systems. We have applied the method to study C_{60}. We find that oxygen chemisorbs over the carbon-carbon double bond, weakening it in the process. The dependence of bond lengths and vibrational frequencies on electron doping is stronger than in intercalated graphite, suggesting a stronger electron-phonon coupling.

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