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C₆₀ as a Faraday cage

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Endohedral fullerenes have been proposed for a number of technological uses, for example, as a nanoscale switch, memory bit and as qubits for quantum computation. For these technology applications, it is important to know the ease with which the endohedral atom can be manipulated using an applied electric field. We find that the Buckminsterfullerene (C₆₀) acts effectively as a small Faraday cage, with only 25% of the field penetrating the interior of the molecule. Thus influencing the atom is difficult, but as a qubit the endohedral atom should be well shielded from environmental electrical noise. We also predict how the field penetration should increase with the fullerene radius. © 2004 American Institute of Physics. [DOI: 10.1063/1.1640783]

Shortly after the discovery of the Buckminsterfullerene, it was proposed that the hollow carbon molecule could act as a cage for an atom: placing an atom inside the cage is called *endohedral doping*.^{1–5} One proposed use of endohedrally doped C₆₀ is as a memory storage device: if the endohedral atom could be moved about inside the cage between two stable positions, the position of the atom could encode the state of the device. The small size of the molecule would lead to a very high bit density compared with that in present day memory circuits. Another proposed use for the endohedral fullerenes N@C₆₀ and P@C₆₀ is as qubits for quantum computation— the group V atoms are chosen because they retain their atomic character once inside the cage. For such systems it is important that decoherence times be sufficiently long, and the C₆₀ cage might be expected to isolate the atom inside from unwanted interactions with the surrounding material.

Here we shall study lithium-doped C₆₀ (Li@C₆₀ for short) as a prototype endohedral fullerene: our conclusions will apply to any endohedral atom and to the higher fullerenes as well. It is known^{6,7} that when lithium is placed inside C₆₀, at room temperature it can move freely on the sphere of radius 1.4 Å within the fullerene. In Fig. 1, the uppermost curve shows the total energy (TE) versus lithium position along our *z* axis—the line of symmetry which passes through the center of a pentagon (C₅)—and one can see the minima at $z = \pm 1.4$ Å. Other directions give similar curves. There are some slight differences between different points on the sphere, but these barriers to transport are very small: the largest we find is 0.04 eV, which is the same order of magnitude as the error in our *ab initio* total energy calculations. The calculations here and those in the following use density functional theory (DFT) with the B3-LYP exchange-correlation functional,⁸ and a Gaussian basis set. A question of major technical interest is whether the trapped atom can be easily influenced by applying an external electric field, for example, by using a scanning tunneling microscope (STM); this is what we study in this letter. We note that a lithium atom transfers approximately one electron to the cage⁹ and becomes positively charged, so such a field should have

some influence on its motion. To investigate this, we applied an external electric field along a fivefold axis and calculated the total energy of the Li@C₆₀ system as a function of the atomic position with all cage atoms held fixed. In Fig. 1 we plot the total energy TE(*z*,*E*) of the system versus position *z* of the lithium atom for four different values of applied electric field, $E \approx 0, 2, 4$ and 8 V/nm. From the graph we see that the degeneracy between the up-field and down-field minima is broken by the field applied, but it is noteworthy that the difference in energy Δ TE between these two local minima is quite small. For example, for the highest applied field of $E = 8.23$ V/nm, and a lithium atom with $q = 1e$ (e =proton charge), by neglecting the cage one would find a difference in energy between the old equilibrium positions of Δ TE = $q E d = 1 \times 8.23 \times 0.28 = 2.3$ eV, while from the graph one reads a difference of 0.45 eV. This small difference leads to small forces on the lithium atom, meaning that the atom will be difficult to manipulate inside the cage.

The simplest way to understand this reduction in force in our *ab initio* DFT calculations is to suppose that the C₆₀ molecule acts as a partial *Faraday cage*, that shields the atom trapped inside from the majority of the field applied. To justify this, we note that by using the Hellmann–Feynman theorem and the subsequent reasoning in Ref. 10 (essentially

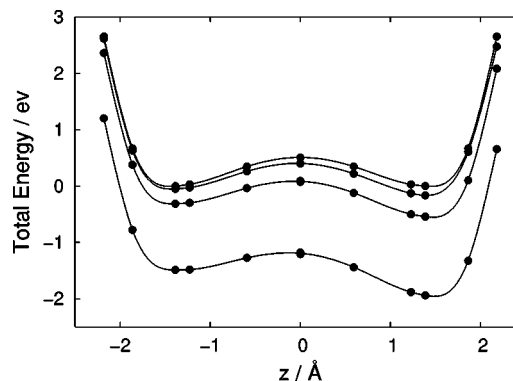


FIG. 1. Total energy of the molecular system in an applied electric field, as we vary the position of the lithium atom along the fivefold symmetry line. We calculate this energy for four different strengths of applied field E : from top to bottom $E = 0, +2.05, +4.11$ and $+8.23$ V/nm. Zero energy is chosen to be the total energy when the atom is at the C₅ energy minimum at $z = \pm 1.4$ Å and $E = 0$.

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integration by parts) we can express the total force $F_z(z, E) = -(\partial TE / \partial z)(z, E)$ on the atomic nucleus as

$$\mathbf{F} = eZ_{\text{Li}}(\mathbf{E}_{\text{applied}} + \mathbf{E}_{\text{electrons}} + \mathbf{E}_{\text{cage nuclei}}), \quad (1)$$

where Z_{Li} is the atomic number of lithium. That is, the force on the nucleus can be thought of as coming from the electric field applied plus the electrostatic field of all the charges in the system. By separating $\mathbf{E}_{\text{electrons}}$ spatially into cage and atomic components $\mathbf{E}_{\text{electrons}} = \mathbf{E}_{\text{cage electrons}} + \mathbf{E}_{\text{atom electrons}}$ and combining the electronic and nuclear cage fields, we see that the force on the lithium atom is given to good approximation by

$$\mathbf{F} = q_{\text{Li}}(\mathbf{E}_{\text{applied}} + \mathbf{E}_{\text{cage}}), \quad (2)$$

where $\mathbf{E}_{\text{cage}}$ is the field of the nuclei and electrons on the cage, and q_{Li} is the net charge on the atom ($\approx 1e$). Thus, it is the *total* electric field $\mathbf{E}_{\text{total}} = \mathbf{E}_{\text{applied}} + \mathbf{E}_{\text{cage}}$ acting on net charge q_{Li} of the atom that determines force $\mathbf{F}$. Then one can simply understand the reduced force by saying that the field applied polarizes the cage, and creates an induced dipole $\mathbf{p}_{\text{induced}} = \alpha(z)\mathbf{E}_{\text{applied}}$ whose field mostly cancels the field applied inside the cage; here $\alpha(z) = -\partial^2 TE / \partial E^2$ is the polarizability of the endohedral system. The high density of polarizable carbon $2p_z$ electrons on the cage leads to a high value of α for the fullerene, and in this limit the shielding approaches metallic behavior. The positively charged lithium atom then feels this reduced total field; we can estimate $E_{\text{inside}}/E_{\text{applied}} \approx 0.45/2.3 = 0.2$. Furthermore, from our $TE(z, E)$ data we find $\alpha(z) = 72.8 \text{ \AA}^3$, a constant to good approximation [the standard deviation of $\alpha(z)$ over 11 atomic positions z is $0.3 \text{ \AA}^3$] and close to the experimental value of $\alpha = 76.5 \pm 8.0 \text{ \AA}^3$ (Ref. 11) for undoped C_{60} . This constant value indicates that most of the dipole moment induced is due to the 360 carbon cage electrons, and little is due to charges on the lithium or the electron donated to the cage: the shielding is truly a C_{60} property, and is independent of the endohedral atom chosen. Our calculations show that even at the strongest field we apply ($E = 8.23 \text{ V/nm}$) we are in the linear response regime. Thus a fixed fraction of the field applied will penetrate through to the interior of the cage to act on *any* endohedral atom: all we need know about the atom is its net charge.

To investigate this interesting shielding effect further, we took C_{60} on its own, with no atom inside, and immersed it in an external electric field of magnitude 8.23 V/nm along the fivefold axis. We then calculated the total electric field inside the buckyball in order to see how much got through the cage. Even at zero applied field there is a background cage field $\mathbf{E}_0(\mathbf{r})$ present inside the hollow, so we subtract this from the total field to get the change in field $\Delta\mathbf{E}(\mathbf{r})$ when the external field is applied. We found this to be reduced to 25% of the magnitude of the applied field, verifying explicitly that C_{60} is a small Faraday cage. Furthermore, the field inside is *constant* in magnitude and direction over a large spherical region inside the cage, centered at the C_{60} center and of radius $2 \text{ \AA}$. Now, since the magnitude of the shielding depends on the response of the valence electrons to the field applied, it might be expected to depend on the number of polarization functions included in the atomic basis set for carbon. To check convergence and estimate an error we performed three sepa-

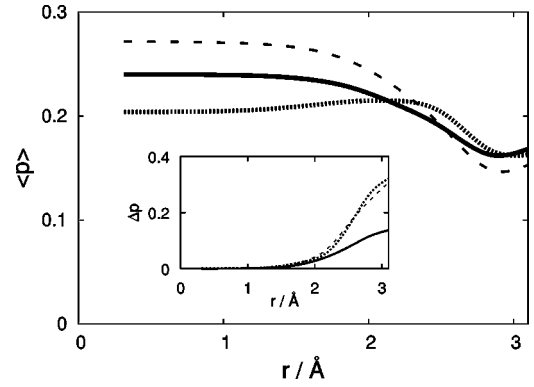


FIG. 2. Average fraction $\langle p \rangle$ of applied field that penetrates the interior of the cage, as a function of the radius of the ball over which we average. This is shown for three calculations using TZVPP (dashed line), TZP (solid line) and cc-pVTZ (dotted line) basis sets. In the inset we show the standard deviation Δp .

rate C_{60} shielding calculations, each with a different carbon Gaussian basis set.¹² Our value of 25% is an average of the three shielding values, and we estimate an error of $\pm 5\%$. To quantify the constant nature of the internal field, in Fig. 2 we show how the average of the *field penetration* $p = \Delta E_z / E_{\text{applied},z}$ and its standard deviation Δp varies with the radius of the ball we average over; the ball here is always centered around the cage center. The main fact here is that the standard deviation is small, so the field is constant over the ball of radius $2 \text{ \AA}$. Beyond a radius of $2.5 \text{ \AA}$ the standard deviation of the shielding is as great as the shielding itself, because the ball has started to include substantial amounts of the $2p_z$ valence charge of the cage, and one can no longer usefully speak of a constant shielding effect. In Fig. 3 we plot the equipotentials and electric field vectors on a plane containing the C_5 axis which passes through a vertex of the pentagon surrounding the axis: one can see the reduced constant internal field.

We can understand the constancy of the internal field by modeling the buckyball as a hollow spherical dielectric shell.¹³ When a uniform external field is applied to such a shell, the field inside the hollow is constant, and is reduced from the field outside by a fraction p that depends on the

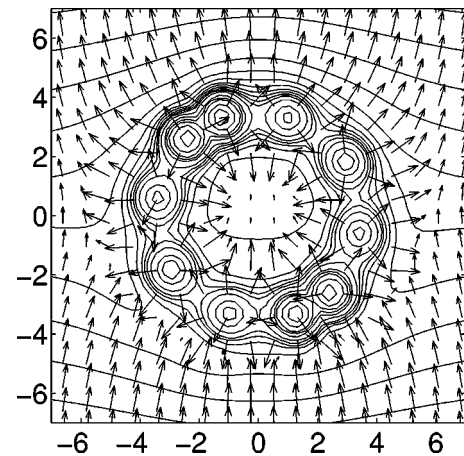


FIG. 3. Equipotentials and field vectors of $\Delta\mathbf{E}$ on our cut plane. The vertical direction is the C_5 axis, along which a field of 8.23 V/nm is applied, and values of the axis are in $\text{\AA}$. There are strong fields near the atoms; for clarity, field vectors longer than 10 V/nm were reduced to this length.

relative dielectric constant ϵ_r of the shell material and the ratio a/b of the inner and outer radii of the shell. Explicitly, the fraction of field p that penetrates to the interior is given by

$$p = \frac{9\epsilon_r}{(2\epsilon_r + 1)(\epsilon_r + 2) - 2(\epsilon_r - 1)^2 a^3/b^3}, \quad (3)$$

and the polarizability α (Gaussian units) is given by

$$\alpha = \frac{(2\epsilon_r + 1)(\epsilon_r - 1)}{(2\epsilon_r + 1)(\epsilon_r + 2) - 2(\epsilon_r - 1)^2 a^3/b^3} (b^3 - a^3). \quad (4)$$

To indicate how our model may be directly applied, we note that in the high ϵ_r limit $\alpha \rightarrow b^3$. Two experimental values for α are 76.5 ± 8.0 (Ref. 11) and $1000 \text{ \AA}^3$.¹⁴ By taking cube roots one can immediately work out effective outer radius values b of 4.24 and 10 $\text{\AA}$, respectively. Given that the radius of the C_{60} cage is 3.5 $\text{\AA}$, and that the $2p_z$ electrons might be expected to extend $\sim 1 \text{ \AA}$ above the nuclear radius, one can use our model to quickly show that $1000 \text{ \AA}^3$ is too high, and that of $76.5 \text{ \AA}^3$ is very plausible.

By fitting to experiment and our shielding calculation one can extract parameters for the model. Assuming $a = 3.5 - \Delta$ and $b = 3.5 + \Delta$, we solve Eqs. (3) and (4) to obtain $\epsilon_r = 18$ and $\Delta = 1.04 \text{ \AA}$. This is a simple model, but we can use it to perform quick estimates of the shielding and polarizability of fullerenes of all sizes; we note that it should be equally applicable to the shielding behavior of carbon nanotubes. One fact that the model enables us to deduce immediately is that the percentage of field that penetrates a fullerene should increase linearly and slowly with the fullerene radius r , growing at the rate of 2% per $\text{\AA}$. This linear formula holds for radii $r \leq 10 \text{ \AA}$; for larger r some downward curvature in the graph of $p(r)$ is evident. Thus larger fullerenes would enable the endohedral atom to be manipulated with greater ease, and as such might be more useful as switches and memory devices, while on shielding grounds C_{60} itself is preferable for quantum computers since it isolates the atom from electrical interaction with the surrounding material; due to the long range of Coulomb interaction this can be a major source of decoherence. Another experimental problem which has been noted with endohedral C_{60} occurs due to the high α

value of the cage. When one tries to manipulate the atom by applying a field $\mathbf{E}$ from a STM tip, the high cage polarizability means that the field has to be increased to large magnitudes in order to try to penetrate the cage, but then the induced dipole moment $\mathbf{p} = \alpha \mathbf{E}$ becomes so large that the force due to the gradient of the field $\mathbf{F}_{\text{cage}} = \mathbf{p} \cdot \nabla \mathbf{E}$ lifts the C_{60} off the surface and pulls it to the tip; this effect is useful for manipulation of the fullerene's position, but limits the voltages that can be applied to electrically address the dopant atom's position. One strategy by which to try to circumvent this is to use larger fullerenes. However, our model predicts that, although the field penetration would increase if larger fullerenes were used, the polarizability increases faster, so the ratio of the two forces $\mathbf{F}_{\text{Li}}/\mathbf{F}_{\text{cage}}$ would only deteriorate as the cage radius is increased.

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