

On the energy spectrum of the C_{60}^- fullerene anion

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Abstract

It is shown that the C_{60}^- fullerene anion has a hydrogen-like energy spectrum.

The electron affinity of carbon is 1.26 eV , while the electron affinity of the C_{60} fullerene molecule is 2.65 eV . [1]:[2] This large increase in electron affinity can not be accounted by any theory of chemical bonding.

Typically,[3] these theories start with an atomic-like π -type orbital for the added electron, and proceed by taking advantage of the neighbouring carbon atoms on the surface of the fullerene molecule for lowering the electron energy. The building blocks of the starting orbital resemble, more or less, the carbon unoccupied p_z -atomic orbital. From symmetry requirements it is found that the ground-state of the added electron is three-fold degenerate and belongs to the t_{1u} -representation of the icosahedral symmetry group of the molecule. These states are thereafter employed for constructing the energy bands of the alkali (A)-doped fullerides A_nC_{60} , yielding a conducting band for the notoriously insulating A_4C_{60} phase. Small distortions are then invoked, both at the molecular and the crystalline level, to lift part of degeneracy by Jahn-Teller effect. However, by such type of approaches, the binding energy of the added electron is always much smaller than its on-site energy, and, therefore, the electron affinity of the fullerene molecule could never reach as large a value as more than twice that of the carbon atom.

The fullerene molecule is practically a spherical molecule of radius $R_0 = 3.5 \text{ \AA}$. An electron delocalized over the surface of such a molecule will induce a polarization charge $z = +e$, where $-e$ is the electron charge. We may consider in first approximation that this charge is uniformly distributed over the surface of the molecule. The energy levels of the electron are, therefore, to be obtained by solving the Schrodinger equation with the potential energy

$$\begin{aligned} V(r) &= -ze/R_0 \quad , \quad \text{for } r < R_0 \quad , \\ V(r) &= -ze/r \quad , \quad \text{for } r > R_0 \quad . \end{aligned} \quad (1)$$

We shall use the atomic units $a_H = \hbar^2/me^2 = 0.53 \text{ \AA}$ (Bohr radius) and $e^2/a_H = 27.2 \text{ eV}$, where m is the electron mass and \hbar is Planck's constant; in addition we put $\hbar = 1$, so that $m = e^2 = 1$. The solution is of the form $R(\rho)Y_{lm}(\theta, \varphi)$, where Y_{lm} are the spherical harmonics and $\rho = r/R_0$. It is well-known that the radial wavefunctions inside the sphere are given by

$$R_{kl}(\rho) = \rho^l \left(\frac{1}{\rho} \frac{\partial}{\partial \rho} \right)^l \frac{\sin k\rho}{\rho} \quad , \quad (2)$$

where $l = 0, 1, 2, \dots$ is the azimuthal quantum number (angular momenta $\hbar l(l+1)$) and $k^2 = 2(zR_0 - \varepsilon)$, $\varepsilon = -ER_0^2$, E being the energy, $-zR_0 < E < 0$. It is also known that these functions are related to the Bessel functions $J_{l+1/2}(k\rho)$. Outside the sphere the radial wavefunctions are of the form $F(\rho)e^{-\sqrt{2\varepsilon}\rho}$, where $F(\rho)$ are polynomials of rank n . It is easy to find out that the spectrum is given by

$$\varepsilon_n = (zR_0)^2 / 2n^2 \quad , \quad n = 1, 2, 3, \dots \quad (3)$$

and that there are three types of solutions listed below:

For $l \leq n - 1$

$$F_{nl}^{(1)}(\rho) = \sum_{s=l}^{n-1} \left(-\frac{n}{2zR_0} \right)^{n-s-1} \frac{(n-l-1)!(n+l)!}{(s-l)!(l+s+1)!(n-s-1)!} \rho^s \quad ; \quad (4)$$

For $l \geq n$

$$F_{nl}^{(2)}(\rho) = \sum_{s=l-1}^{n-1} \left(\frac{n}{2zR_0} \right)^{n-s-1} \frac{(l-s-1)!(n+l)!}{(l-n)!(l+s+1)!(n-s-1)!} \rho^s \quad , \quad (5)$$

and

$$F_{nl}^{(3)}(\rho) = \sum_{s=l-1}^{-n-1} \left(-\frac{n}{2zR_0} \right)^{-n-s-1} \frac{(l-n)!(n+l+1)!}{(l-s)!(l+s+1)!(-n-s-1)!} \rho^s \quad . \quad (6)$$

At this point it is worth comparing these results with those corresponding to the Coulomb potential. In the case of the Coulomb potential, with wavefunctions finite at $\rho = 0$, the electron is pushed further and further away from the origin with increasing l ; however, this is not possible beyond a certain extent, since the Coulomb potential is attractive enough at the origin, and the electron has to stay there around in order to take advantage of this attraction. Consequently, the azimuthal quantum number l is bounded from above in the case of the Coulomb potential, as it is well known. In the present case, the potential is not attractive enough at the origin, and l may take any positive, integer value. In addition, in the $\rho > 1$ region the second solution of the radial Schrodinger equation is also allowed, namely that solution which diverges at the origin; it is given by (5) and (6) above. It reveals the fact that the electron tends to stay closer and closer to the surface of the sphere, in order to diminish its potential energy.

The general solution to our problem for a given n is therefore a superposition over l, m and the two radial wavefunctions $F_{nl}^{(2,3)}$ for $\rho > 1$ and $l \geq n$. It is easy to see that the boundary condition at $\rho = 1$, *i.e.* the continuity of the logarithmic derivative, is not satisfied for $l \leq n - 1$. Therefore, the states with low angular momenta are not allowed. On the contrary, the boundary condition is satisfied by a suitable choice of superposition coefficients for $l \geq n$, due precisely to the presence of the two independent functions $F_{nl}^{(2,3)}$ for $\rho > 1$ in this case.

Summarizing this calculation we may say, therefore, that the energy spectrum of the electron is

$$E_n = -\frac{z^2}{2n^2} \quad , \quad n = 1, 2, 3, \dots \quad , \quad (7)$$

and its wavefunctions are (up to a constant)

$$\Psi_{nlm} = R_{nl}(\rho)Y_{lm}(\theta, \varphi) \quad , \quad \text{for } \rho < 1 \text{ and } l \geq n \quad , \quad (8)$$

and

$$\Psi_{nlm} = \left[A_{nlm} F_{nl}^{(2)}(\rho) + B_{nlm} F_{nl}^{(3)}(\rho) \right] e^{-\sqrt{2\varepsilon_n}\rho} Y_{lm}(\theta, \varphi) \quad , \quad \text{for } \rho > 1 \text{ and } l \geq n \quad , \quad (9)$$

where R_{nl} is given by (2) for $k_n^2 = 2(zR_0 - \varepsilon_n)$ and

$$\begin{aligned} A_{nlm} &= \frac{R_{nl}(1) \left[F_{nl}^{(3)'}(1) - \sqrt{2\varepsilon_n} F_{nl}^{(3)}(1) \right] - R'_{nl}(1) F_{nl}^{(3)}(1)}{F_{nl}^{(2)}(1) F_{nl}^{(3)'}(1) - F_{nl}^{(3)}(1) F_{nl}^{(2)'}(1)} e^{\sqrt{2\varepsilon_n}} \quad , \\ B_{nlm} &= \frac{R'_{nl}(1) F_{nl}^{(2)}(1) - R_{nl}(1) \left[F_{nl}^{(2)'}(1) - \sqrt{2\varepsilon_n} F_{nl}^{(2)}(1) \right]}{F_{nl}^{(2)}(1) F_{nl}^{(3)'}(1) - F_{nl}^{(3)}(1) F_{nl}^{(2)'}(1)} e^{\sqrt{2\varepsilon_n}} \quad . \end{aligned} \quad (10)$$

Apart from the orbital degeneracy the spectrum is otherwise non-degenerate, as is well known.

The ground-state energy a and the energy a_1 of the first excited state are therefore given by (7) as $z^2/2n^2 = a$ and $z^2/2(n+1)^2 = a_1$; whence we get $n = \left(\sqrt{a/a_1} - 1 \right)^{-1}$. The solution n of this equation should be an integer. The ground-state energy is the electron affinity $a = 2.65 \text{ eV}$. On the other hand, we know from absorption experiments[4],[5] the excitation energy 1.16 eV , which corresponds to $a_1 = 1.49 \text{ eV}$. Using these data we get from the above equation $n = 2.997$, *i.e.* $n = 3$, and $z = 1.32$. One can check easily that $zR_0 < 2n^2$ for these values. Hence one may conclude that the energy spectrum of the C_{60}^- anion is given by $E_n = -z^2/2n^2$ with $z = 1.32$ and $n = 3, 4, 5, \dots$. The next excited states have the energies $E_5 = -0.95 \text{ eV}$, $E_6 = -0.66 \text{ eV}$, $E_7 = -0.48 \text{ eV}$, etc ($E_3 = -a = -2.65 \text{ eV}$, and $E_4 = -a_1 = -1.49 \text{ eV}$). The corresponding absorption lines have, however, very low intensities. For the sake of reference we give here the ionization potential 7.6 eV of C_{60} .

The orbital degeneracy of the spectrum derived above may indicate that highly-charged fullerene anions may also exist. Indeed, suppose that we add another electron to C_{60}^- , and neglect for the moment the Coulomb repulsion between the two electrons. We may also assume that both electrons induce a total charge z close to unity, and take $z = 1.32$, as found above. Indeed, in a quasi-classical picture the two electrons stay at the opposite ends of the fullerene diameter in order to minimize their Coulomb repulsion, so each of them will "see" an induced charge $z \sim 1$. The two electrons will have each the fundamental state corresponding to $n = 3$, as derived before, and antiparallel spins; the energy of the fullerene anion C_{60}^- is therefore lowered further by 2.65 eV , so that the fullerene dianion C_{60}^{2-} has a fundamental state of energy $2 \cdot 2.65 \text{ eV}$; however, we must subtract the Coulomb repulsion, which in this case is at least $e^2/2R_0 \approx 2 \text{ eV}$, so that the second electron has lost in fact an energy smaller than $2.65 \text{ eV} - 2 \text{ eV} = 0.65 \text{ eV}$. This value is rather close to $0.1 \text{ eV} - 0.4 \text{ eV}$, computed for the electron affinity of the anion C_{60}^- by means of pseudopotentials[6].

A comment is in order here. The value $z = 1.32$ obtained above for the charge induced on the surface of the fullerene molecule, greater than $z = 1$ expected for the isolated molecule, may include the polarization effects of the surrounding environment (solution in the case of Ref.4, solid argon in the case of Ref.5). This environment, as well as the small irregularities of the electron density on the surface of the fullerene molecule, may also split the orbitally degenerate energy levels, leading to a fine structure of the spectrum; weak absorptions may then be detected, accompanying the main absorption at 1.16 eV . The spectrum may also have an even richer fine structure, if one considers the coupling of the added electron to the molecular vibrations. It is also worth mentioning in this context that the rather large values obtained here for the quantum

numbers n and l indicate that the non-uniformity of the charge induced on the molecule surface is small, validating thus our assumption. At the same time, for these values of the quantum numbers we should expect a rather important spin-orbit coupling, which is another source (and, probably, the main one) for the multiplet structure of the spectrum. An interesting type of coupling will also arise from the magnetic field generated by the induced currents on the surface of the rotating molecule, which will affect both the orbital momentum of the electron and its spin; for the former case this is an $\mathbf{L} \cdot \mathbf{l}$ -type of coupling, where \mathbf{L} is the angular momentum of the molecule and \mathbf{l} is the electron angular momentum. However, the magnitude of this coupling is extremely small, due, especially, to the large momentum of inertia of the fullerene molecule.

It might also be worth commenting in this context upon the temptation of employing the hydrogen-like wavefunctions obtained here for the C_{60}^- anion for constructing the energy bands of the alkali-doped fullerenes. This would not be advisable, since the fullerene molecules in the alkali-doped fullerenes are close enough to one another (the distance between two neighbouring C_{60} 's is $\sim 3 \text{ \AA}$) as to disturb considerably the electron spectrum derived here for a single, isolated molecule. However, it might be exactly this proximity effect that could reasonably open another way for constructing the energy bands of these compounds. Indeed, one may assume that the hybridization of the atomic-like orbitals of the neighbouring carbon atoms on pairs of adjacent fullerene molecules are responsible for the electronic structure of these solid-phase compounds. As it is easy to see, these orbitals were not subject to other symmetries except those of the (face-centered cubic) crystalline structure. One may start with the unoccupied carbon orbitals $2p_z$, $3s$, $3p$, etc, which would lead to non-degenerate bands, predicting thereby that the $A_n C_{60}$ fullerenes with $n = 2, 4, 6$ are insulating, as pointed out experimentally. Preliminary calculations show also that $n = 6$ seems to be the highest stable compound in this class.

Finally, we may add that similar calculations as those reported here for C_{60}^- can also be performed for the C_{70}^- anion. The quasi-ellipsoidal shape of the C_{70} molecule leads to interesting effects regarding the degeneracy of the spectrum.

References

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