Coulomb and exchange interactions in C_{60}^{n-}

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Semiempirical modified-neglect-of-differential-overlap (MNDO) quantum chemistry calculations are performed for the negative ions of an isolated C_{60}. The value computed for the first electron affinity is in excellent agreement with experiment. MNDO predictions of the energies of the low-lying states of C_{60}^{2-} and C_{60}^{3-} allow us to extract an effective on-site repulsion $U_0 \sim 3$ eV, and a direct exchange interaction $K \sim 50$ meV for C_{60}. These values are used to estimate the effective on-site repulsion and dielectric constant of solid C_{60}, with results in good agreement with experiment. A similar approach is used to determine "partially" screened parameters appropriate to a model of K_3C_{60}. We find that both the on-site ($U_0 \sim 1.3$ eV) and near-neighbor ($V \sim 0.3$ eV) Coulomb terms are significant relative to the bandwidth ($W \sim 0.6$ eV).

I. INTRODUCTION

The intramolecular properties of C_{60} figure prominently in many of the mechanisms proposed to explain superconductivity in the alkali-doped fullerides.[1-3] Both conventional electron-phonon mechanisms,[4,5] in which the high-frequency (800–1600 cm^{-1}) tangential modes in C_{60} are utilized to explain the high critical temperatures observed (~ 30 K in Rb_3C_{60}), and purely electronic mechanisms[6] have been studied. While these two viewpoints are quite different, they share the feature that the origin of the pairing interaction is intramolecular in nature. In order to generate a net attractive pair interaction, the bare Coulomb repulsion between a pair of electrons in C_{60} must be overcome. The magnitude of this repulsion is therefore an important number to know.

In this work, we report the results of semiempirical quantum chemistry calculations designed to address the stability of the anionic states of an isolated, gas-phase C_{60}. We find that the results can be mapped onto an effective "atomic" model in which the states of C_{60}^{n-} are generated by occupying an "effective" p orbital, characterized by an on-site electron repulsion (Pariser's γ_{aa}, or Hubbard's U) of order ~ 3 eV and a direct exchange interaction K of ~ 50 meV. This model is then extended to a lattice, and estimates of the screened parameters appropriate to M_3C_{60} are made.

II. RESULTS

We begin by studying the electronic states of isolated C_{60} anions. C_{60}^- is known to be bound by 2.65 eV in the gas phase.[7] While the C_{60}^{2-} ion has also been observed,[8,9] it is not known whether this species is a long-lived metastable or actually bound with respect to $C_{60}^- + e^-$.

We choose to study this system theoretically with the modified neglect of differential overlap (MNDO) approximation.[10] This method was used by Stanton and Newton[11] to obtain the heats of formation, geometry,

normal modes, and infrared (IR) intensities for C_{60}. The predictions of MNDO for the two distinct bond distances in C_{60} (1.474 and 1.400 Å) are close to those derived from both experimental ^{13}C NMR data[12] (1.45 and 1.40 Å) and *ab initio* calculations which include correlation corrections through second order in perturbation theory (1.446 and 1.406 Å).[13] The IR absorption frequencies calculated are, on average, 15% higher than those observed,[14] but MNDO typically overestimates vibrational frequencies by about 10%.[15] MNDO has been applied by Varma, Zaanen, and Raghavachari[5] to determine the electron-phonon coupling in C_{60}^-, and by Bakowies and Thiel, and Raghavachari and Rohlfing[16] to study a number of other large carbon clusters.

The lowest unoccupied molecular orbital in C_{60}, the orbital which accepts the additional electrons present in the anions, is triply degenerate transforming as t_{1u} in the icosahedral point group (I_h). Note that the Cartesian vectors $\hat{x}, \hat{y}, \hat{z}$ also transform as t_{1u} in I_h and so for the purpose of characterizing the available electronic states we may think of the acceptor orbital as p-like. Thus we represent the three components of the unoccupied t_{1u} orbital as $t_{1u(x)}, t_{1u(y)},$ and $t_{1u(z)}$.

The ground state of C_{60} is a closed shell, ^1A_g state. Addition of a single electron yields a $^2T_{1u}$ state whose energy relative to C_{60} defines the acceptor orbital site energy ε. Several years ago, local-density-functional (LDA) calculations[17] predicted that the $^2T_{1u}$ state should be bound by 2.7 eV relative to $C_{60} + e^-$. Recent photodetachment experiments on C_{60}^- by Wang *et al.*[7] do, in fact, find that C_{60}^- is bound by 2.65 eV, in excellent agreement with the LDA prediction. Using the MNDO approximation considered in the present work we find a binding energy of 2.68 eV, in very good agreement with the previous results.

Both the LDA and MNDO theoretical estimates refer to "vertical" binding energies, in which the geometry of C_{60}^- is fixed at that of C_{60}. Because the $^2T_{1u}$ ground state of C_{60}^- is triply degenerate, it will be subject to a first-order Jahn-Teller interaction. The direct product

$T_{1u} \times T_{1u}$ reduces to $A_g + T_{1g} + H_g$ in I_h. Of these, vibrational modes of h_g symmetry are Jahn-Teller active. There are eight independent modes of h_g symmetry in C_{60}^-, and so the vibronic motion on the lower adiabatic sheet will, in principle, be a quite complicated affair involving a 40-dimensional coordinate space. The minimum on this surface must lie below the vertical energy by some Jahn-Teller stabilization energy. A portion of this multidimensional energy surface has been investigated by de Coulon, Martins, and Reuse[18] using LDA. They find, as expected, a very small stabilization energy of the order of 25 meV.

The electronic states of the doubly charged anion are of particular interest in that they reveal the magnitude of the effective gas-phase Coulomb and exchange interactions. The configuration t_{1u}^2 gives rise to $^3T_{1g}$, ^1H_g, and ^1A_g electronic states in strict analogy with the low-lying ^3P, ^1D, and ^1S multiplets of the carbon (p^2) atom. At the MNDO level of approximation, again fixing the geometry to be that of C_{60}, we find the $^3T_{1g}$ electronic state to be the ground state of C_{60}^{2-}. This species should also be Jahn-Teller active. Its energy is -2.28 eV relative to C_{60} and it is therefore bound with respect to ejection of two electrons. It lies slightly higher in energy (~ 0.4 eV) than $C_{60}^- + e^-$. This is in agreement with recent calculations using LDA by de Coulon, Martins, and Reuse[18] and by Pederson and Quong.[19] de Coulon, Martins, and Reuse find a second electron affinity of $+0.26$ eV, while Pederson and Quong find $+0.11$ eV. These both refer to "vertical" affinities as does the MNDO result. However, Pederson and Quong have also considered the influence of geometrical relaxation and find that it decreases the second affinity from $+0.11$ to $+0.04$ eV. Accounting for spin polarization decreases it further to $+0.02$ eV. However, when a "generalized gradient approximation" improvement to the LDA is applied, the second affinity is increased to 0.3 eV once again. It therefore appears that the calculations to date suggest that C_{60}^{2-} is slightly unbound relative to C_{60}^-. On the experimental side, Hettich, Compton, and Ritchie[8] have observed C_{60}^{2-} in the gas phase and infer that it is bound relative to $C_{60}^- + e^-$. Given the errors inherent in the calculations, it may

indeed be slightly bound; on the other hand, if it is slightly unbound as the calculations suggest, the t_{1u} character of the acceptor orbital should lead to a centrifugal barrier in the detachment channel $C_{60}^{2-} \rightarrow C_{60}^- + e^-$ and a metastable species might be observed. Photodetachment experiments would resolve these absolute stability questions.

The excited states of C_{60}^{2-} are also of interest. A MNDO calculation on the single configuration $t_{1u(x)}^2$ finds it to lie at -2.18, or ~ 0.1 eV above the triplet state. These state energies are summarized in Table I.

III. A MULTIPLET MODEL

The calculations described to this point allow us to extract the effective Coulomb and exchange parameters characterizing the acceptor orbital. Multiplet theory yields energy expressions for the triplet and singlet states of C_{60}^{2-},

$$E(^3T_{1g}) = 2\varepsilon + U_{xy} - K_{xy} = 2\varepsilon + U_0 - \tfrac{5}{3}K , \qquad (1)$$

$$E(^1H_g) = \begin{cases} 2\varepsilon + U_{xy} + K_{xy} \\ 2\varepsilon + U_{xx} - K_{xy} \end{cases} = 2\varepsilon + U_0 + \tfrac{1}{3}K , \qquad (2)$$

$$E(^1A_g) = 2\varepsilon + U_{xx} + 2K_{xy} = 2\varepsilon + U_0 + \tfrac{10}{3}K , \qquad (3)$$

where the Coulomb interactions are defined by

$$U_{xy} = (xx, yy) = U_{xz} = U_{yz} , \qquad (4)$$

$$U_{xx} = (xx, xx) = U_{yy} = U_{zz} , \qquad (5)$$

$$K_{xy} = K_{xz} = K_{yz} = \cdots = K , \qquad (6)$$

with

$$(ij, kl) = \int \int \varphi_i(1)\varphi_j(1) \left[\frac{1}{r_{12}} \right] \varphi_k(2)\varphi_l(2) , \qquad (7)$$

and U_0 refers to the multiplet averaged Coulomb repulsion

$$U_0 = U_{xy} + \tfrac{2}{3}K_{xy} = U_{xx} + \tfrac{4}{3}K_{xy} . \qquad (8)$$

Now, the configuration $t_{1u(x)}^2$ is an average of the ^1H_g and ^1A_g states with energy $2\varepsilon + U_{xx}$. Given $\varepsilon = -2.68$ eV from the first electron affinity, we may determine the remaining parameters. We find $U_0 = 3.14$ eV and $K_{xy} = 0.03$ eV. The magnitudes of these parameters seem quite reasonable. For example, if the motion of the two additional electrons in C_{60}^{2-} were perfectly correlated so that they always remained as far apart as possible on the surface of a sphere, then the effective repulsion should be given approximately by e^2/R, where $R \sim 7$ Å is the diameter of C_{60}. This classical estimate gives $U = 2.1$ eV and might be expected to be a lower bound.

Given these parameters, we can predict the energies of the states of C_{60}^{3-}. The t_{1u}^3 occupancy gives rise to ^4A_u, ^2H_u, and $^2T_{1u}$ multiplets which are formally similar to the ^4S, ^2D, and ^2P states of the nitrogen (p^3) atom. The ^4A_u state should lie lowest with an energy

$$E(^4A_u) = 3\varepsilon + 3(U_0 - \tfrac{5}{3}K) = 1.23 \text{ eV} . \qquad (9)$$

TABLE I. C_{60}^{n-} energies.

	State	MNDO	Ab initio SCF[a]
C_{60}	^1A_g	0.0	0.0 (0.0)
C_{60}^-	$^2T_{1u}$	-2.68	-0.92 (-2.67)
C_{60}^{2-}	$^3T_{1g}$	-2.28	1.05 (-2.45)
	^1H_g	-2.18[b]	1.27 (-2.23)
	^1A_g		1.59 (-1.91)
C_{60}^{3-}	^4A_u	0.91	5.91 (0.66)
	^2H_u		
	$^2T_{1u}$		

[a]A. H. H. Chang, W. E. Ermler, and R. M. Pitzer, J. Phys. Chem. **95**, 9288 (1991). The parenthetical entries are the results of applying a 1.75-eV correlation energy correction to the energy of each state (see text).

[b]The energy of the single configuration $t_{1u(x)}^2$. This corresponds to a configuration with energy $2\varepsilon + U_{xx} = E(^1H_g) + 1/2E(^1A_g)$.

When the full MNDO calculation is performed one finds $E({}^4A_u)=0.91$ eV. This reasonable agreement demonstrates the internal consistency of the model, but more importantly, it shows that the parameters are not dramatically changed when the other electrons in the σ and π framework are allowed to adjust to the presence of a third electron. A dependence on the charge state of ~ 0.1 eV in U_0 is suggested by this test. Finally, we note that unlike the ground states of $C_{60}{}^-$ and $C_{60}{}^{2-}$, the ${}^4A_u$ ground state of $C_{60}{}^{3-}$ is not subject to a first-order Jahn-Teller effect.

Based on the good agreement between the calculated and observed first electron affinity, we estimate the Coulomb parameters are probably reliable to within ± 0.2 eV. Additional evidence is provided by the recent *ab initio* self-consistent-field (SCF) calculations on the anions of C_{60} by Chang, Ermler, and Pitzer.[20] Their results are also presented in Table I. The *ab initio* SCF absolute binding energies are, as expected, too small. Note that the error between the *ab initio* SCF first electron affinity and experiment is ~ 1.75 eV. This corresponds to the correlation energy between an additional electron and the remaining electrons of C_{60}. If one assumes a similar correction for each of the additional electrons in $C_{60}{}^{2-}$ and $C_{60}{}^{3-}$, one generates the "correlation corrected" SCF results shown parenthetically in Table I. It can be seen that with the correlation correction the *ab initio* SCF results are in good agreement with the present semi-empirical work. These "corrected" *ab initio* results can also be fit to the multiplet model, and one finds $U_0=3.07$ eV, $K_{xy}=0.11$ eV. Once again, an internal consistency check on the energy predicted for the ${}^4A_u$ state using Eq. (7) is in good agreement with the directly computed result in Table I. The *ab initio* model parameters are therefore also largely independent of charge state.

The MNDO parameters and the "correlation corrected" first-principles parameters are summarized in Table II. There is excellent agreement between the two sets. Note that since *ab initio* SCF calculations typically overestimate the direct exchange interaction, the value of 0.11 eV is not necessarily more reliable than the 0.03 eV determined by MNDO. A magnitude of 50 meV seems a reasonable compromise.

After this paper was initially submitted for publication, we became aware of LDA calculations with aims similar to ours. The LDA does not distinguish the multiplet structure discussed above, and the energies of $C_{60}{}^{n-}$ presumably refer to a state average; the LDA U should therefore be compared with the multiplet average U_0. Pederson and Quong[19] and de Coulon, Martins, and Reuse[18] find $U_0=3.0-3.1$ eV within the LDA, in excel-

lent agreement with the value of ~ 3.1 eV determined here. Andropov, Gunnarson, and Jepsen[21] find a slightly smaller value, $U_0=2.6$ eV. The overall agreement among the various calculations is good, and the gas-phase value would appear to be a few tenths either side of $U_0 \sim 3$ eV.

IV. SCREENING CONSIDERATIONS

We turn now to estimates of the Coulomb interactions in the condensed phase. Band-structure calculations[22,23] clearly show that the alkali metal acts primarily as a donor of electrons to the t_{1u} acceptor orbitals and mediates an effective hopping interaction t between two fullerenes. This suggests that the cations can be eliminated from the problem and that a model in which each $C_{60}{}^{3-}$ is represented by the three components of a p orbital might prove interesting to study. The band which originates from the t_{1u} orbitals is half-filled for $C_{60}{}^{3-}$ and narrow. LDA calculations yield a bandwidth $W \sim 0.6$ eV.[22,23] Magnetization measurements of the normal-state susceptibility and NMR measurements of the ${}^{13}C$ spin-relaxation time imply an even narrower band, $W \sim 0.2$ eV.[24] The bandwidth is related to the effective hopping interaction via the approximation $W \cong 2zt$, where $z=12$ is the number of nearest neighbors in the fcc lattice. Clearly, in the absence of additional screening in the condensed phase, the Coulomb and exchange interactions are significant relative to the bandwidth. In addition to the on-site Coulomb and exchange interactions of magnitude ~ 3 eV and ~ 50 meV, respectively, the near-neighbor repulsion term V is also significant. The distance between two C_{60} centers in K_3C_{60} is ~ 10 Å which implies $V=e^2/10$ Å$=1.4$ eV. To summarize, the unscreened electron repulsion parameters are both much greater than the bandwidth; $U/W \sim 5$ and $V/W \sim 2$ if the LDA bandwidth is used. These ratios are even larger (by a factor of 3) if the experimentally inferred bandwidth is used.

In order to have an appropriate model with which to study the electronic properties of the condensed phase, we must address how these parameters are screened in the solid. The direct exchange interaction is known to be poorly screened in a solid because it requires inefficient multipolar screening mechanisms.[25] It should remain in the vicinity of 50 meV. It is tempting to ignore this term in formulating a model to extend to the infinite lattice, but as Lof *et al.* have noted,[26] the total multiplet splitting in $C_{60}{}^{3-}$ is of the order of 5 K ~ 0.25 eV, and it is therefore a significant fraction of the bandwidth. In addition, the direct exchange interaction may be important for understanding the ferromagnetic behavior observed by Allemand *et al.*[27] in the compound $TDAE_1C_{60}$.

Unlike the direct exchange, the values of U and V will be strongly screened in the metal. There are two types of response that we must consider. The first is the metallic screening brought about by the finite bandwidth originating from the conduction band. This should be captured naturally by the hopping integral t when the model Hamiltonian is studied on the lattice. The second response is interband in character and cannot be recovered in a simple model which reduces the electronic degrees of free-

TABLE II. Multiplet model parameters for C_{60} (eV).

	MNDO	"Corrected" *ab initio* SCF
ε	-2.68	-2.67
U_0	3.14	3.07
K	0.03	0.11

dom of C_{60} to a single "effective" orbital. In order to estimate this contribution, we examine the limit in which the bandwidth goes to zero. Recall that the effective U is the energy needed to remove an electron from one $C_{60}{}^{3-}$ and place it on another at infinite separation; i.e.,

$$U = E(C_{60}{}^{4-}) + E(C_{60}{}^{2-}) - 2E(C_{60}{}^{3-}) .   \qquad (10)$$

In the solid, both the $C_{60}{}^{2-}$ and $C_{60}{}^{4-}$ species so generated will be stabilized by the electronic polarization of neighboring icosahedral-C_{60} anions. Thus,

$$U_s = U - 2E_{pol} ,   \qquad (11)$$

where E_{pol} is the electronic polarization energy accompanying removal or addition of a charge. The latter should be, approximately,

$$E_{pol} = \frac{ze^2\alpha}{2R^4} ,   \qquad (12)$$

where α is the $C_{60}{}^{3-}$ polarizability, and R is the distance between the C_{60} centers. Note that Eq. (12) supposes that only the nearest neighbors (z of them) contribute to the polarization energy. Pederson and Quong have computed the polarizability of $C_{60}{}^{n-}$ using finite-field techniques within the LDA and find $\alpha = 82$ Å^3 for C_{60} and $\alpha = 98$ Å^3 for $C_{60}{}^{3-}$. The former is in excellent agreement with the value for C_{60} estimated by Hettich, Compton, and Ritchie[8] ($\alpha \sim 80$ Å^3). Using the polarizability appropriate for C_{60}, we find $E_{pol} \sim 0.7$ eV and $U_s \sim 1.6$ eV. Lof et al.[26] have recently extracted an "experimental" U for C_{60} from an analysis of the Auger spectrum. They deduce $U = 1.6 \pm 0.2$ eV, in excellent agreement with the present work. For K_3C_{60} the larger polarizability of $C_{60}{}^{3-}$ should be used, and the screened repulsion is slightly smaller $U_s \sim 1.3$ eV. As opposed to using Eq. (12), Pederson and Quong explicitly construct an fcc lattice of polarizable particles and evaluate the energy as a function of the charge state, and find $U_0 = 1.27$ eV. The nearest-neighbor approximation apparently works fairly well in this case, presumably due to the steep R^{-4} dependence of the polarization energy.

Similarly, the nearest-neighbor repulsion should be approximately

$$V_s = \left[\frac{1}{\varepsilon}\right] V ,   \qquad (13)$$

where

$$\varepsilon = \frac{\left[1 + \dfrac{8\pi N\alpha}{3}\right]}{\left[1 - \dfrac{4\pi N\alpha}{3}\right]}   \qquad (14)$$

is the dielectric constant, and N the C_{60} concentration. Evaluation of this expression using the polarizability appropriate for neutral C_{60} yields $\varepsilon \sim 3.6$ and $V_s \sim 0.4$ eV. The static dielectric constant of C_{60} has been measured by various means,[28] and the results range from 3.9–4.4, in fair agreement with our estimate of 3.6. If the value

TABLE III. Partially screened parameters for K_3C_{60} (eV).	
t	0.025
U	1.3
V	0.3
K	0.05

$\alpha = 98$ Å^3 appropriate for $C_{60}{}^{3-}$ is used, then $\varepsilon \sim 5.0$ and $V_s \sim 0.3$ eV. The explicit lattice sum utilized by Pederson and Quong gives $\varepsilon \sim 4.75$ and $V_s \sim 0.3$ eV.

The "partially" screened parameters appropriate to M_3C_{60} are summarized in Table III.

V. CONCLUSIONS

The electronic states of $C_{60}{}^{n-}$ computed with the MNDO approximation are well described by an effective "single orbital" model. The MNDO results are in excellent agreement with experiment for the electron affinity of C_{60} in the gas phase. The calculations have been used to extract an effective on-site Coulomb repulsion $U_0 = 3.1$ eV, and a direct exchange interaction $K = 0.03$ eV. These parameters are in good agreement with first-principles SCF calculations empirically corrected for correlation contributions which give $U_0 = 3.1$ eV, $K = 0.11$ eV. They are also in good agreement with LDA predictions of U_0 which give ~ 3 eV, although one LDA calculation yields a slightly lower value of 2.6 eV. The LDA cannot address the direct exchange parameter K. MNDO and ab initio SCF calculations yield values of 0.03 and 0.11 eV, respectively, and we suggest a compromise of $K \sim 50$ meV.

The results of the gas-phase calculations have been used to predict the effective U and the dielectric constant for the insulating material C_{60}, both of which are in reasonable agreement with recent experiments. The results suggest that the model Hamiltonian below might capture many of the interesting electronic properties of M_3C_{60}.

$$H = \sum_{i,m} \varepsilon_i n_{im} + \sum_{i,j,m,n} t_{i,j,m,n} a_{im}^\dagger a_{in} + \sum_{i,m,n} \frac{U}{2} n_{im}(n_{in} - 1)$$
$$+ \sum_{i \neq j,m,n} \frac{V}{2} n_{im} n_{jn} - \sum_{i,m \neq n} K a_{im}^\dagger a_{in} a_{im}^\dagger a_{in} .   \qquad (15)$$

Here, i and j label sites, and m and n label the spatial and spin components of the p orbital on each site. Note that the first four terms define an extended Hubbard or Pariser-Parr-Pople model, while the final term adds the one-center exchange interaction. On-site electron-phonon coupling terms such as those suggested in the literature could be added to the site energy operator in Eq. (15). Our best estimates of the parameters appropriate for M_3C_{60} are given in Table III.

Perhaps the most important conclusion of this work is that the magnitudes of the "partially" screened parameters of Table III are comparable to or large compared with either the LDA bandwidth, $W \sim 0.6$ eV, or the experimentally inferred value $W \sim 0.2$ eV (the hopping in-

tegral in Table III has been estimated from the LDA bandwidth; the rationale for this is that the experimental bandwidth may reflect renormalization effects which arise from the large Coulomb terms). This does not necessarily mean that these "partially screened" parameters are inconsistent with an electron-phonon mechanism for superconductivity. Using a somewhat different approach, Gunnarsson and Zwicknagl[29] find a very efficient intraband metallic screening which significantly reduces the effective repulsive interactions. In addition, retardation effects may play a significant role in overcoming the rather large Coulomb repulsion found in this work. Given these cautions, however, it is interesting to note that the bare near-neighbor repulsion V is a significant fraction ($\sim \frac{1}{4}$) of the on-site Hubbard U. This term tends

to drive charge-density fluctuations, as opposed to the spin-density fluctuations governed by U. The effect of V is amplified in the fcc lattice in which there are a large number of near neighbors. This may be relevant to the mechanism for superconductivity in these materials. For example, in their study of a negative U model, Zhang, Ogata, and Rice[30] have pointed out that formation of charge-density waves is frustrated in the fcc lattice and singlet superconductivity is favored instead. In that work, the focus was on electron-phonon coupling driving the charge disproportionation, as opposed to the intersite electron repulsion discussed here. Finally, the direct interaction in Eq. (15) may lead to some interesting phenomena, such as tendency toward local spin polarization.[26]

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