

Lawrence Berkeley National Laboratory

Recent Work

Title

Spin Density Waves, Charge Density Wave and Polarizabilities of C₆₀ in the Pariser-Parr-Pople Model

Permalink

<https://escholarship.org/uc/item/3fv1p5j6>

Journal

Journal of Chemical Physics, 98(8)

Authors

Willaime, F.
Falicov, L.M.

Publication Date

1992-11-03



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials Sciences Division

Submitted to Journal of Chemical Physics

Spin Density Wave, Charge Density Wave and Polarizabilities of C_{60} in the Pariser-Parr-Pople Model

F. Willaime and L.M. Falicov

November 1992



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

LOAN COPY
Circulates
for 4 weeks

Bldg. 50 Library.
Copy 2

LBL-33096

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

**Spin Density Wave, Charge Density Wave and Polarizabilities
of C_{60} in the Pariser-Parr-Pople Model**

F. Willaime and L.M. Falicov

Department of Physics
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

November 1992

**Spin Density Wave, Charge Density Wave and Polarizabilities
of C₆₀ in the Pariser-Parr-Pople Model**

F. WILLAIME* and L.M. FALICOV

Department of Physics, University of California, Berkeley, CA 94720

and

Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

ABSTRACT

The Pariser-Parr-Pople Hamiltonian is investigated on a single C₆₀ molecule in the Hartree-Fock approximation. The effect of on-site and two-site electron-electron interactions on the stability of states other than the normal paramagnetic state is studied. In particular: (i) a spin-density wave state, with a structure similar to that of the classical ground state of the antiferromagnetic Heisenberg Hamiltonian ; and (ii) a charge density wave state which occurs for weakly screened two-site interactions. Linear and nonlinear optical properties are also calculated. With the Finite Field method and the Møller-Plesset correction in second order, a linear polarizability of 325.5 a.u. and a second hyperpolarizability of 5.87×10^{-36} esu are found.

* *Permanent address: Section de Recherches de Métallurgie Physique, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette Cedex, France.*

1. INTRODUCTION

The recently synthesized new class of organic molecular solids composed of the soccerball shaped C_{60} molecule have revealed unexpected and unusual electric and magnetic properties [1,2]. Superconductivity upon doping with alkali-metals is the most spectacular. As expected from the highly delocalized π -electron cloud of the spherical C_{60} molecule, large linear [3-7] and nonlinear [7-9] responses have been measured.

Most of the physics involved in these properties originates at the scale of a single molecule, with strong electron-electron interactions. It has motivated several studies of this new molecule with simple model Hamiltonians which include these interactions. In this context, the Hubbard model has been used to support a purely electronic mechanism for superconductivity. By treating the on-site electron-electron repulsion in second-order perturbation theory it was found that pair-binding [10] occurs for (U/β) larger than a critical value [11]. However the effect is extremely sensitive to two-site interactions. The latter drastically reduce or suppress the weak pair-binding effect found in their absence [12].

In a recent series of papers, spin structures have been investigated on the C_{60} molecule and other fullerenes within the Hubbard model, *i.e.*, neglecting once more two-site interactions. First, Coffey and Trugman studied the large- U limit of the Hubbard model, *i.e.*, the antiferromagnetic Heisenberg Hamiltonian [13]. They found that the classical ground state has a non trivial topology where the spins on each pentagon have the structure of the ground state of an isolated pentagon (*i.e.*, all spins are coplanar and are related by a rotation of $(4\pi/5)$ about a given axis); the spins on all bonds connecting two pentagons are exactly antiparallel. The possibility of having such magnetic structures, *i.e.*, non vanishing spin-spin correlations at short range, has been further supported by Quantum-Monte-Carlo simulations on the one-band Hubbard model at half filling on a C_{60} molecule [14] as well as by the study of the exact $S=1/2$ ground state for the antiferromagnetic Heisenberg Hamiltonian on a truncated tetrahedron (C_{12}). [15] No experimental evidence of this magnetic structure has been reported as yet.

As measured from different experiments the refraction index is about 2.0 in the C_{60} solid, and this value is theoretically well understood [16,17]. On the other hand, measurements of non-linear optical properties are characterized by large dispersion. In particular, the reported value of the third order susceptibility $\chi^{(3)}$ ranges from 7×10^{-12} esu to 2×10^{-10} esu. Because of the large size of the molecule, this property are difficult to calculate at present from first-principle studies [17]. Semi-empirical models can therefore be useful tools to get a better understanding of this effect. With the use of a time-dependent coupled-perturbed Hartree-Fock approach (in a molecular-orbital method with intermediate neglect of diatomic differential overlap) a value of $\chi^{(3)}$ two to

three orders of magnitude smaller than the experimental number was calculated [18]. A similar value was obtained from a simpler calculation based with a tight-binding Hamiltonian for the σ and π electrons [19].

The purpose of this contribution is to present the study of the C_{60} molecule with the so-called Pariser-Parr-Pople (PPP) Hamiltonian -- also called extended Hubbard Hamiltonian -- in the Hartree-Fock approximation. The stability of the Spin-Density Wave (SDW) ground state -- the analogue to the ground state of the classical Heisenberg Hamiltonian -- is studied. In particular the influence of the two-site interactions is analyzed. A Charge-Density Wave (CDW) ground state, which appears for weakly screened interactions, is investigated as well. The linear polarizability and the second hyperpolarizability are calculated within various approximations.

Section 2 is devoted to the presentation of the method: the PPP and the Hartree-Fock Hamiltonians, and the various approximations used to calculate the polarizabilities (Hückel, Sum-Over-States, and Finite Field methods and the Møller-Plesset correction). Section 3 contains the results of the study of the stability of the SDW and the CDW. The results for the linear polarizability and second hyperpolarizability in C_{60} are presented in Section 4 and compared to experiments and other calculations. The linear polarizability in C_{70} is also calculated. The main results and conclusions are summarized in Section 5. The appendix contains a proof of the reduction of the coefficients of the fourth-rank tensor of the *static* second hyperpolarizability to a single independent coefficient in a system with icosahedral symmetry.

2. METHOD

2.A The PPP-Hamiltonian

The Pariser-Parr-Pople Hamiltonian considered here is restricted only to the 60 outer electrons of the C_{60} molecule [20]. It can be written as

$$H = H_1 + H_2 \quad (1)$$

The one-particle term,

$$H_1 = -\beta_1 \sum_{\langle ij \rangle \sigma} c_{i\sigma}^\dagger c_{j\sigma} - \beta_2 \sum_{(ij)\sigma} c_{i\sigma}^\dagger c_{j\sigma} \quad (2)$$

is the usual Hückel Hamiltonian. The first sum runs over all distinct $\langle ij \rangle$ bonds connecting two hexagons and the second sum runs over all distinct bonds (ij) that connect two pentagons; $c_{i\sigma}^\dagger$ and

$c_{i\sigma}$ are the one-particle creation and destruction operators. The term H_1 alone gives a good picture of the one-electron energy levels in C_{60} as shown in early studies [21]. The two-particle term,

$$H_2 = \frac{1}{2} \sum_{i\sigma} \gamma_{ii} n_{i\sigma} n_{i-\sigma} + \frac{1}{2} \sum_{i \neq j} \gamma_{ij} n_i n_j, \quad (3)$$

includes on-site and two-site Coulomb interactions. Here $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ and $n_i = n_{i\sigma} + n_{i-\sigma}$ are the usual number operators. The ultraviolet optical spectrum of C_{60} has been studied by means of this Hamiltonian with configuration interaction [22].

2.B The Hartree-Fock Hamiltonian

The following form of the unrestricted Hartree-Fock approximation of (1), which allows three-dimensional arrangements of the spins, was used:

$$\begin{aligned} H_{HF} = H_1 &+ \sum_{i\sigma} \gamma_{ii} (\langle c_{i\sigma}^\dagger c_{i\sigma} \rangle c_{i-\sigma}^\dagger c_{i-\sigma} - \langle c_{i\sigma}^\dagger c_{i-\sigma} \rangle c_{i-\sigma}^\dagger c_{i\sigma}) \\ &- \frac{1}{2} \sum_{i\sigma} \gamma_{ii} (\langle c_{i\sigma}^\dagger c_{i\sigma} \rangle \langle c_{i-\sigma}^\dagger c_{i-\sigma} \rangle - \langle c_{i\sigma}^\dagger c_{i-\sigma} \rangle \langle c_{i-\sigma}^\dagger c_{i\sigma} \rangle) \\ &+ \sum_{i \neq j, \sigma\sigma'} \gamma_{ij} (\langle c_{i\sigma}^\dagger c_{i\sigma} \rangle c_{j\sigma'}^\dagger c_{j\sigma'} - \langle c_{i\sigma}^\dagger c_{j\sigma'} \rangle c_{j\sigma'}^\dagger c_{i\sigma}) \\ &- \frac{1}{2} \sum_{i \neq j, \sigma\sigma'} \gamma_{ij} (\langle c_{i\sigma}^\dagger c_{i\sigma} \rangle \langle c_{j\sigma'}^\dagger c_{j\sigma'} \rangle - \langle c_{i\sigma}^\dagger c_{j\sigma'} \rangle \langle c_{j\sigma'}^\dagger c_{i\sigma} \rangle), \quad (4) \end{aligned}$$

where $\langle A \rangle$ is the ground-state expectation value of operator A and is determined self consistently. In this approach the ground state -- in the first-quantization picture -- is a single determinant of one-electron states. The latter are defined by 120 *complex* coefficients in the basis of the $\{i\sigma\}$ states. For a given self-consistent-field (SCF) solution the three components of the expectation value of the spin on site i are given by

$$\begin{aligned} \sigma_i^x &= \frac{1}{2} (\langle c_{i\uparrow}^\dagger c_{i\downarrow} \rangle + \langle c_{i\downarrow}^\dagger c_{i\uparrow} \rangle) , \\ \sigma_i^y &= \frac{1}{2i} (\langle c_{i\uparrow}^\dagger c_{i\downarrow} \rangle - \langle c_{i\downarrow}^\dagger c_{i\uparrow} \rangle) , \\ \sigma_i^z &= \frac{1}{2} (\langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle - \langle c_{i\downarrow}^\dagger c_{i\downarrow} \rangle) . \end{aligned} \quad (5)$$

2.C Polarizability

When an external uniform electric field, F , acts upon a centrosymmetric molecule, the change in energy is written -- according to the Bloembergen expansion [23] for the induced dipole moment in powers of the electric field -- as

$$E = E^{(0)} - \frac{1}{2} \sum_i \sum_j \alpha_{ij} F_i F_j - \frac{1}{4} \sum_i \sum_j \sum_k \sum_l \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (6)$$

where α and γ are respectively the second-rank tensor of the linear polarizability and the fourth-rank tensor of the second hyperpolarizability. The summations i, j, k , and l run over the cartesian axes (x,y,z); $E^{(0)}$ is the unperturbed energy; and F_i is the component of the electric field in the i direction.

Because of icosahedral symmetry, the number of independent coefficients in α and in γ in the static limit for the C_{60} molecule is reduced to one each. In addition to the trivial relations which apply to a totally symmetric tensor, the non-zero coefficients are related by (see appendix)

$$\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = \alpha \quad (7)$$

$$\gamma_{xxxx} = \gamma_{yyyy} = \gamma_{zzzz} = 3 \gamma_{xxyy} = 3 \gamma_{xxzz} = 3 \gamma_{yyzz} = \gamma \quad (8)$$

Equations (7) and (8) define the scalar quantities α and γ used hereafter. In other words, the response of C_{60} to a uniform external electric field is perfectly isotropic up to fourth order. For an electric field of strength F , applied in any direction, the energy expansion of equation (6) now reads:

$$E = E^{(0)} - \frac{1}{2} \alpha F^2 - \frac{1}{4} \gamma F^4 \dots \quad (9)$$

The linear and second hyperpolarizability of the present model can be calculated within various approximations. First, when H_2 is neglected in (1), the exact results for α and γ can be obtained either by treating the additional term in the Hamiltonian,

$$H_3 = - \sum_i e F \cdot r_i \quad (10)$$

in standard Rayleigh-Schrödinger perturbation theory at the second and fourth order, or by diagonalizing directly $(H_1 + H_3)$ for various field strengths. The values obtained by this method are referred to as the *Hückel* values.

The *Summation Over States* (SOS) approach [24] is based on the result of the SCF solution of the HF Hamiltonian in the absence of an external field. Perturbation theory, as described above, is then used to calculate the polarizabilities. The effective one-electron Hamiltonian H_{HF} replaces H_1 . In this approach there is a lack of self-consistency between the eigenfunctions of the Hartree-Fock operator and the orbitals defining that operator when an electric field is applied.

In the *Finite Field* (FF) method, the Hartree-Fock, self-consistent-field solution of $(H+H_3)$ is determined for various strengths of the external electric field [24]. The result can be improved by treating in perturbation theory the difference between the exact Hamiltonian $(H+H_3)$ and the corresponding HF Hamiltonian, in the so-called *Møller-Plesset* perturbation theory [23,25]. The Møller-Plesset correction in the second order (MP-2) is used in this contribution.

For the very sensitive case of the Møller-Plesset calculations the numerical stability was checked carefully. A convergence criterion on the density-matrix elements of typically 10^{-12} for $F \approx 0.1 \text{ V \AA}^{-1}$ was required; α and γ were derived numerically according to (6) from four different strengths of the external electric field and a maximum strength of $F = 0.1 \text{ V \AA}^{-1}$ (the first level crossing occurs at $F \approx 0.8 \text{ V \AA}^{-1}$).

The response of the C_{60} *solid* to an external electric field can be reasonably modeled as that of an assembly of isolated dipoles. For such a system, the polarizabilities of the isolated molecule and the bulk linear susceptibility, $\chi^{(1)}$, and the third-order nonlinear susceptibility, $\chi^{(3)}$ can be related [26] taking into account the Lorentz local-field correction

$$\chi^{(1)} = \frac{N \alpha}{1 - (4\pi/3) N \alpha} \quad , \quad (11)$$

and

$$\chi^{(3)} = \frac{N \gamma}{(1 - (4\pi/3) N \alpha)^4} \quad , \quad (12)$$

where N is the density of molecules in the crystal. Equation (11) is the Clausius-Mossotti relation.

2.D Parameters

The standard values for the hopping integrals β_1 and β_2 and their ratio are typically $2.0 \text{ eV} \leq \beta_1 \leq \beta_2 \leq 2.5 \text{ eV}$ and $1 < \beta_2/\beta_1 < 1.3$ [27]. In the present calculation these parameters are chosen to be $\beta_2/\beta_1=1.1$, and $\beta_2=2.5 \text{ eV}$.

The recommended value for the on-site Coulomb repulsion, γ_{ii} , in the PPP approach is the difference between the ionization potential and the electronic affinity [28], *i.e.*, 11.13 eV for carbon atoms [22]. In Section 3 below γ_{ii} is taken as a free parameter, and in Section 4 the value $\gamma_{ii}=11.13 \text{ eV}$ is taken for calculating polarizabilities.

The choice of the two-site Coulomb repulsions, γ_{ij} , is more difficult. The screening caused by the σ -electrons reduces them from their pure coulombic value (e^2/r_{ij}). Different empirical potentials have been proposed in the literature to account for this effect. They usually interpolate the effective repulsion integral between two electrons on the same site, γ_{ii} , and the coulombic

dependence at large distances. For benzene, the PPP model has been solved exactly and the four γ_{ij} have been fitted to the five best known experimental energy levels [29]. This result is used here to test three empirical potentials, those of Ooshika [30], Mataga and Nishimoto [31], and Ohno [32]. The values of γ_{ij} calculated for these empirical potentials, as well as the coulombic values for benzene are listed in table I, and compared to the results of Visscher and Falicov [29]. Clearly, the Ohno potential is the most suitable for benzene. It is therefore expected to be also well suited for C_{60} as an *isolated* molecule or even in the solid state for the undoped *insulating* state. However the environment in which the C_{60} molecule is placed is likely to modify value and shape of the screening. This modification will be particularly sensitive in the doped fulleride M_3C_{60} , which is a metal, and where metallic screening reduces drastically the importance of long-range interactions.

An additional parameter, λ , is introduced in the original expression for Ohno's potential. This parameter controls the strength of the screening and can be seen as a normalized distance:

$$\gamma_{ij} = \frac{e^2}{(R^2 + r_{ij}^2)^{1/2}} \quad (13)$$

where $R = \lambda R_0$ and $R_0 = (e^2 / \gamma_{ii})$. This single formulation has the advantage of making the connection between three particular cases : (i) $\lambda=0$ is the pure coulombic repulsion ; (ii) $\lambda=1$ corresponds to the original Ohno potential (*i.e.*, $\gamma_{ij} \rightarrow \gamma_{ii}$ when $r_{ij} \rightarrow 0$) ; and $\lambda = \infty$ gives $\gamma_{ij} = 0$ for $i \neq j$, *i.e.*, the PPP model reduces to the Hubbard model.

The geometrical parameters of the truncated icosahedral structure of C_{60} are the two nearest-neighbor distances, r_1 for the bond connecting two hexagons, and r_2 for the bonds connecting two pentagons. Throughout this calculation, their values have been fixed to the ones recently determined indirectly by NMR experiments [33,34] on the C_{60} *solid* at 77 K, *i.e.*, $r_1 = 1.45 \text{ \AA}$ and $r_2 = 1.40 \text{ \AA}$. For the molecular density, N , in (11) and (12), the experimental value [35] at room temperature is taken (*i.e.*, a lattice parameter $a = 14.16 \text{ \AA}$).

Table II summarizes the geometrical and Hamiltonian parameters used in the calculation.

3. PHASE DIAGRAM

In the non-interacting limit ($\gamma_{ii} / \beta \rightarrow 0$ and λ finite) the ground state is the normal non-magnetic state ($\sigma_i = 0$ on each site), with charge uniformly distributed over all sites. At large

(γ_{ii} / β), one can expect the ground state to be magnetic, with quantum spins arranged in a way similar to that of the classical ground state of the antiferromagnetic Heisenberg Hamiltonian [13]. The latter solution is thus a good candidate to construct the initial density matrix of the SCF-HF procedure. By doing so, for any value of λ , and for values of γ_{ii} larger than a critical values, $\gamma_c(\lambda)$, the SCF solution obtained has exactly the same structure, *i.e.*, a generalized SDW structure. Whenever this SDW solution exists, its HF energy is lower than that of the normal state, and it is stable with respect to small random perturbations on the density matrix. The magnitude of the spins is the same on all sites, and goes continuously to zero as γ_{ii} approaches $\gamma_c(\lambda)$ (see figure 1). The critical values of γ_{ii} for $\lambda = 0, 1$, and $+\infty$ are 14.85 ± 0.05 , 13.2 ± 0.1 and 6.4 ± 0.1 eV respectively. The general dependence of γ_c on λ can be understood as follows: the relevant parameter for magnetic ordering is not the absolute value of γ_{ii} but rather its value relative to the average two-site interaction, γ_{ij} , namely $(\gamma_{ii} - \bar{\gamma})$, where $\bar{\gamma}$ is an average [36] over the γ_{ij} ($i \neq j$). The set of values of λ and γ_{ii} where the SDW state exists with a finite amplitude has been determined and is shown in figure 2. This SDW solution breaks the icosahedral symmetry. This symmetry-breaking is related to the fact that, by definition, the HF solutions use only one Slater determinant. From any SDW solution, in addition to the configurations obtained by a global rotation of all spins, another configuration can be obtained by the spin-inversion operation $\vec{\sigma}_i \rightarrow -\vec{\sigma}_i$. Therefore it is obvious (as in all antiferromagnets) that linear combinations of states with pairs of spins inverted are better trial functions [14, 15, 37].

For vanishing screening ($\lambda=0$), and for γ_{ii} lower than a critical value, SCF-HF solutions with a generalized CDW can be obtained. These solutions are characterized by a non-uniform distribution of the charge. Various locally stable distributions were found, but the most stable one has the highest symmetry. The non-trivial symmetry of the latter is shown in figure 3 and contains all the even representations (symmetries) of the icosahedral group : A_g, T_{1g}, T_{3g}, G_g (x2) and H_g . This non-trivial symmetry is caused by the frustration arising in the five-fold rings. As in the SDW solution, this CDW solution has always an HF energy lower than that of the normal state. This kind of configuration is driven by a considerable reduction of the Madelung energy. However this reduction is only sizeable for low values of λ , *i.e.*, for very large values of the two-site repulsions. Although the values of λ and γ_{ii} where this solution appears are of limited physical interest, they have been determined for the sake of completeness and are shown in figure 3. In particular, for $\lambda=0$, a critical value of $\gamma_{ii}=14.85$ eV, identical to that obtained for the SDW, was found. This instability towards a CDW is not particular to C_{60} ; an even a larger region of instability is found when using the same parameters on a single graphite layer.

The present work is not a systematic study of all the SDWs and CDWs that can possibly

exist on C_{60} . Only the domain of existence of one particular SDW and one CDW have been determined [13]. Other structures, in particular mixed SDW-CDW states, may exist.

4. POLARIZABILITIES

The linear polarizability and the hyperpolarizability for the present model, calculated with various approximations, are presented in this section and compared with experimental results and other calculations. The parameters are: $\gamma_{ii}=11.13$ eV, and three different values of the screening parameter, $\lambda=0$ (no screening), $\lambda=1$ (Ohno screening) or $\lambda=2$ (in SDW regime).

4.A Linear Polarizability

The only experimental results available for the linear response of C_{60} are from measurements in the *solid*. Expressed in terms of linear susceptibility, $\chi^{(1)}$, they all agree within about $\pm 10\%$. The refraction index [3-7] is about 2.0 (*i.e.*, $\chi^{(1)} \approx 0.24$ esu). With the Clausius-Mossotti relation (11), the experimental values measured for $\chi^{(1)}$ correspond to a linear polarizability of 530 - 621 au (78.5×10^{-24} esu to 92×10^{-24} esu).

The linear polarizability has been determined, *ab initio*, by means of Hartree-Fock calculations using various basis sets. The result for the largest set (the so-called 6-31G* basis) provides a lower limit [16] of $\alpha = 442.1$ au. Another estimate from first-principle calculations, but with the so-called LDA-GGA approach [17], gave a value of $\alpha = 557.9$ au in excellent agreement with experiments.

In the present model, the simple Hückel value is $\alpha = 1168.9$ au, which is artificially too large because of the neglect of electron-electron interaction. The FF value, with Ohno screening ($\lambda=1$), is 318.9 au. The Møller-Plesset correction in second order produces a small change, to a value of $\alpha = 325.5$ au. The SOS result is $\alpha = 387.8$ au.

From the Hückel and SOS calculations the excitations that contribute the most to the polarizability can be identified. These are from orbitals near the Fermi level, in particular the one-electron $H_g \rightarrow T_{1u}$, $H_u \rightarrow T_{1g}$ and $H_u \rightarrow H_g$ transitions. The H_u is the highest occupied molecular orbital and T_{1u} is the lowest unoccupied molecular orbital. They contribute, in the SOS calculation, 85% of the total value of α (39%, 30% and 16% respectively). A similar conclusion was drawn from the unscreened polarizability calculation of reference 17.

The effect of the λ parameter on α was also examined. For $\lambda=0$ (no screening), the FF value of α is reduced to 252.5 au. For $\lambda = 2$, the FF calculation has been performed both in the metastable normal state (using a restricted Hartree-Fock Hamiltonian) and in the SDW state. The linear polarizabilities are 434.1 and 379.7 au respectively.

The results in the present calculation are very similar to those obtained with similar one-electron Hamiltonians -- *i.e.*, Hückel Hamiltonians for the π -electrons only or tight-binding Hamiltonians for both the π and the σ electrons -- and various approximations. These values range [19,39,40] from $\alpha = 240$ au to $\alpha = 340$ au. A discrepancy with experimental results is therefore common to most semi-empirical calculations. Only the intermediate neglect of diatomic differential overlap with time-dependent coupled-perturbed Hartree-Fock (INDO-TDCPHF) result of reference 18 is in surprisingly good agreement with experiments ($\alpha = 548.7$ au). It is also interesting to notice that the polarizability of C_{60} is essentially that of a classical conducting sphere of radius $R = 3.5 \text{ \AA}$ ($\alpha = 288$ au).

Comparison between experimental and theoretical values of the linear optical properties of C_{60} is shown in Table III. More details on the various calculated values are listed in Table IV.

The linear polarizability of C_{70} has also been calculated with the same Hamiltonian, with the following parameters: $\gamma_{ii} = 11.13$ eV, $\lambda = 1$, and $\beta = 2.5$ eV for all nearest-neighbour bonds. The atomic positions were taken from the optimized geometry of reference 41. With the FF method the values found are $\alpha_{xx} = \alpha_{yy} = \alpha_{//} = 426.0$ au, $\alpha_{zz} = \alpha_{\perp} = 433.9$ au, and $\bar{\alpha} = 428.6$ au. For the sake of comparison, the same calculation for C_{60} with $\beta_1 = \beta_2 = 2.5$ eV yields $\alpha = 331.8$ au. It has been argued [41] that $\bar{\alpha}$ should scale with the number v of atoms in the fullerene. On the other hand, if the polarizability is essentially that of the corresponding sphere or spheroid, then $\bar{\alpha}$ should scale with $v^{3/2}$. In the present calculation, one finds a ratio $\bar{\alpha}(C_{70}) / \bar{\alpha}(C_{60}) = (70/60)^{1.66}$. A similar ratio [16,41] was found from *ab initio* Hartree-Fock calculations using the same basis for C_{60} and C_{70} , namely $\bar{\alpha}(C_{70}) / \bar{\alpha}(C_{60}) = (70/60)^{1.47}$. Both results are close to a scaling of $\bar{\alpha}$ by a factor $v^{3/2}$.

4.B Second Hyperpolarizability

The nonlinear optical properties of C_{60} have been investigated both in the solid and in solution using various techniques with wavelengths from $0.62 \mu\text{m}$ to $1.9 \mu\text{m}$ (see Table V). All measurements showed a very large nonlinear optical response, as expected from the highly delocalized π -electron cloud. The dispersion in the results expressed in terms of the third order susceptibility, $\chi^{(3)}$, ranges from 7×10^{-12} esu to 220×10^{-12} esu, or in terms of the hyperpolarizability, γ , from 3×10^{-34} esu to 9×10^{-33} esu [7-9,42].

For the present model with Ohno screening ($\lambda=1$) the FF value of γ is 4.76×10^{-36} esu. The relative Møller-Plesset correction in second order is larger for γ than for α , and yields a total

value of 5.87×10^{-36} esu. For comparison the SOS and Hückel values of γ are respectively 19.3×10^{-36} esu and 415.2×10^{-36} esu. The SOS method overestimates γ by a factor of 4. The fact that the disagreement between the SOS result and the more rigorous FF result is worse for γ than for α is not surprising and is commonly observed [43]. For $\lambda = 0$ (no screening), the FF value of γ is reduced to 2.7×10^{-36} esu. For $\lambda = 2$, the FF calculation has been performed both in the normal and in the SDW states. Results are 12.6×10^{-36} esu and 55.7×10^{-36} esu respectively. The hyperpolarizability is considerably enhanced by the presence of a SDW.

The numerical stability required to calculate γ is such that *ab initio* calculations have been limited to small molecules [43]. In the C_{60} calculation of reference 17 no nonlinear contributions could be detected. Therefore, the understanding of the large value of γ in C_{60} must for the moment rely only on semi-empirical approaches. In this context, the INDO-TDCPHF method has provided interesting results [18]. The static value of $\gamma = 4.95 \times 10^{-36}$ esu, is very close to that of the present model. Starting from a tight-binding Hamiltonian for σ and π electrons a comparable value of $\gamma = 2.3 \times 10^{-36}$ esu was found [19]. Another tight-binding study [44] for π electrons only, which neglects both the Coulomb interactions and the Lorentz local-field correction, led to a static value of $\chi^{(3)} = 1.22 \times 10^{-12}$ esu. A peak in the third-harmonic generation [44] was also found at $3\omega \approx 2.5$ eV. Experimental and calculated results are listed in Table V.

All calculations from semi-empirical Hamiltonians which take into account Lorentz local-field correction and a reasonable treatment of Coulomb interactions lead to $\gamma \approx 5 \times 10^{-36}$ esu, *i.e.*, two to three orders of magnitude smaller than that inferred from experiments. Although discrepancies between calculated and experimental values of this quantity are not unusual, such a large discrepancy needs further investigation. Possible reasons have been suggested in reference 18. A large dispersion caused by various third-order processes or by wavelength dependence does not seem plausible [18].

5. CONCLUSIONS

A simple PPP-Hamiltonian of the C_{60} molecule that treats *all* Coulomb interactions between π -electrons has been investigated. The stability of the SDW, which is the ground state of the classical Heisenberg model has been studied in the Hartree-Fock approximation. The critical value of the on-site correlation integral, γ_{ii} , below which the SDW vanishes is 6.4 eV when two-site interactions are neglected [45]. When Ohno-type screening of the two-site interactions is included the critical value increases to 13.2 eV. For this particular type of two-site interactions the only SCF-HF solutions found for the model, with the widely accepted value of $\gamma_{ii} = 11.13$ eV, is the normal paramagnetic state. However the possibility of having either a SDW or a soft excitation

mode leading towards this type of instability cannot be excluded from the present model. This type of situation should be favored in a more effectively screened (metallic) environment. For weakly screened interactions, the occurrence of a CDW has also been obtained theoretically.

The study of the optical properties of C_{60} confirmed that this type of semi-empirical model leads to a reasonable, albeit not very accurate, linear polarizability. Furthermore it indicates a scaling of α with $v^{3/2}$ for larger fullerenes. The second hyperpolarizability is found to be two to three orders of magnitudes lower than the experimental values. This large discrepancy requires further investigations.

ACKNOWLEDGMENTS

The authors acknowledge stimulating discussions with E. Artacho, D. Deaven and A. da Silva. FW acknowledges financial support from the Commissariat à l'Energie Atomique (CEA), France. This research was supported at the Lawrence Berkeley Laboratory, by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy, under contract No. DE-AC03-76SF00098.

APPENDIX

In this appendix, the relations between the non-zero components of a fully symmetric fourth-rank tensor, γ_{ijkl} , are derived for a system with icosahedral symmetry. The cartesian axes can be taken along three mutually orthogonal two-fold axes. The $x = 0$, $y = 0$, and $z = 0$ planes are mirrors, and as a consequence the only non-zero coefficients are of the type γ_{ijij} . The [111] direction is a three-fold rotation axis; therefore

$$\gamma_{xxyy} = \gamma_{yyzz} = \gamma_{xxzz} \quad , \quad (A1)$$

and

$$\gamma_{xxxx} = \gamma_{yyyy} = \gamma_{zzzz} \quad . \quad (A2)$$

By noting that the response to a field applied in the direction of any of the 15 two-fold axes is the same, and equal to the one along the x-direction (one of the two-fold axes), for example, one obtains

$$\gamma_{xxyy} = \gamma_{xxxx} / 3 \quad (A3)$$

Relations (A1) to (A3), caused by icosahedral symmetry are those of an isotropic medium. These relations apply in particular to the second hyperpolarizability in the static limit ($\omega = 0$). The dynamical polarizability ($\omega \neq 0$) corresponds to a γ tensor which is no longer fully symmetric.

REFERENCES

- [1] A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T.M. Palstra, A.P. Ramirez, and A.R. Kortan, *Nature* **350**, 600 (1991); M.J. Rosseinsky, A.P. Ramirez, S.H. Glarum, D.W. Murphy, R.C. Haddon, A.F. Hebard, T.T.M. Palstra, A.R. Kortan, S.M. Zahurak, and A.V. Makhija, *Phys. Rev. Lett.* **66**, 2830 (1991).
- [2] P.-M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, J.D. Thompson, *Science* **253**, 301 (1991) ; and R. Blinc, D. Mihailovic, P. Cevc, J. Dolinsek, D. Abramic, B. Zalar, P. Venturini, H. Oshio, P.-M. Allemand, A. Hirsch, and F. Wudl (Preprint 1992).
- [3] W. Krätschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature* **347**, 354 (1990).
- [4] P.L. Hansen, P.J. Fallon, and W. Krätschmer, *Chem. Phys. Lett.* **181**, 367 (1991).
- [5] A.F. Hebard, R.C. Haddon, R.M. Fleming and A.R. Kortan, *Appl. Phys. Lett.* **59**, 2109 (1991).
- [6] S.L. Ren, Y. Wang, A.M. Rao, E. McRae, J.M. Holden, T. Hager, K. Wang, W.T. Lee, J. Selegue and P.C. Eklund, *Appl. Phys. Lett.* **59**, 2678 (1991).
- [7] Z.H. Kalafi, J.R. Lindle, R.G.S. Pong, F.J. Bartoli, L.J. Lingg and J. Milliken, *Chem. Phys. Lett.* **188**, 492 (1992).
- [8] H. Hoshi, N. Nakamura, Y. Maruyama, T. Nakagawa, S. Suzuki, H. Shiromaru, and Y. Achiba, *Jpn. J. Appl. Phys.* **30**, L1397 (1991).
- [9] Y. Wang and L.T. Cheng, *J. Phys. Chem.* **96**, 1530 (1992).
- [10] Pair-binding is said to occur when two noninteracting molecules with $(n+1)$ and $(n-1)$ electrons respectively have lower total energy than two n -electron molecules.
- [11] S. Chakravarty and S. Kivelson, *Europhys. Lett.* **16**, 751 (1991); S. Chakravarty, M.P. Gelfand and S. Kivelson, *Science* **254**, 970 (1991).
- [12] W.E. Goff and P. Philipps, *Phys. Rev. B* **46**, 603 (1992) ; similar results have also been obtained by G.N. Murthy and A. Auerbach (Preprint 1992).
- [13] D. Coffey and S.A. Trugman, *Phys. Rev. Lett.* **69**, 176 (1992).
- [14] R.T. Scalettar, E. Dagotto, L. Bergomi, T. Jolicœur, and H. Monien, (Preprint 1992).
- [15] D. Coffey and S.A. Trugman, LA-UR-92-712 Los Alamos (Preprint 1992).
- [16] P.W. Fowler, P. Lazzeretti and R. Zanasi, *Chem. Phys. Lett.* **165**, 79 (1990).
- [17] A.A. Quong and M.R. Pederson, *Phys. Rev. B* **46**, to appear November (1992); M.R. Pederson and A.A. Quong, (Preprint 1992).
- [18] G.B. Talapatra, N. Manickam, M. Samoc, M.E. Orczyk, S.P. Karna, and P.N. Prasad, *J. Phys. Chem.* **96**, 5206 (1992).

- [19] Y. Wang, G.F. Bertsch, and D. Tomanek, (Preprint 1992).
- [20] R. Pariser and R.G. Parr, J. Chem. Phys. **21**, 767 (1953) ; J.A. Pople, Trans. Faraday Soc **49**, 1375 (1953) ; R. Pariser and R.G. Parr, J. Chem.Phys. **23**, 711 (1955) ; and for a review see *Quantum Theory of Molecular Electronic Structure*, edited by R.G. Parr (W.A. Benjamin, Inc , New York, 1963).
- [21] R.C. Haddon, L.E. Brus and K. Raghavachari, Chem. Phys. Lett. **125**, 459 (1986) ; and M. Osaki and A. Takahashi, Chem. Phys. Lett. **127**, 242 (1986).
- [22] I. László and L. Udvardi, Chem. Phys. Lett. **136**, 418 (1987).
- [23] See for instance E. Perrin, P.N. Prasad, P. Mougeot and M. Dupuis, J. Chem. Phys. **91**, 4728 (1989).
- [24] For a recent review on the SOS and FF methods for calculating polarizabilities see for instance J.-M. André, C. Barbier, V. Bodartn and J. Delhalle, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, vol. 2, edited by D.S. Chemla and J. Zyss, (Academic Press, Orlando, Florida, 1987) p. 137.
- [25] See for instance A. Szabo and N.S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1989), revised first edition, pp. 322, 350, and 377.
- [26] See for instance Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
- [27] V. Elser and R.C. Haddon, Nature **325**, 792 (1987) ; R.B. Mallion, Nature **325**, 760 (1987) ; and E. Manousakis, Phys. Rev. B **144**, 19 (1991).
- [28] R. Pariser, J. Chem. Phys. **21**, 568 (1953).
- [29] P.B. Visscher and L.M. Falicov, J. Chem. Phys. **52**, 4217 (1970).
- [30] Y. Ooshika, J. Phys. Soc. Japan **12**, 1238 (1957).
- [31] N. Mataga and K. Nishimoto, Z. Phys. Chem. NF **13**, 140 (1957).
- [32] K. Ohno, Theoret. Chim. Acta (Berl.) **2**, 219 (1964).
- [33] C.S. Yannoni, P.P. Bernier, D.S. Bethune, G. Meijer and J.R. Salem, J. Am. Chem.Soc **113**, 3190 (1991).
- [34] The result of reference 33 is in agreement with the results of an experimental neutron powder diffraction study on crystalline C₆₀ at 5 K, *i.e.*, $r_1 = 1.455 \text{ \AA}$ and $r_2 = 1.391 \text{ \AA}$ (W.I.F. David, R.M. Ibberson, J.C. Matthewman, K. Prassides, T.J.S. Dennis, J.P. Hare, H.W. Kroto, R. Taylor, and D.R.M. Walton, Nature **353**, 147 (1991)). Calculated values for an *isolated* molecule at *zero temperature* are slightly different; the best published theoretical estimates are $r_1 = 1.448 \text{ \AA}$, and $r_2 = 1.370 \text{ \AA}$ for a self-consistent Hartree-Fock calculation (G.E. Scuseria, Chem. Phys. Lett. **176**, 423 (1991)). For a review on calculated values see also J. Feng, J. Li, Z. Wang and M.C. Zerner, Int. J. Quant. Chem. **37**, 599 (1990).

[35] W.I.F. David, R.M. Ibberson, T.J.S. Dennis, J.P. Hare and K. Prassides, *Europhys. Lett.* **18**, 219 (1992).

[36] The curve of γ_c as a function of λ can in fact be perfectly fitted to the equation

$$\gamma_c(\lambda) - \tilde{\gamma}(\lambda) = 6.4 \text{ eV}$$

where

$$\tilde{\gamma}(\lambda) = x \tilde{\gamma}_{\text{NN}} + (1-x) \tilde{\gamma}_{\text{tot}}$$

with $x = 0.75$. Here $\tilde{\gamma}_{\text{NN}}$ and $\tilde{\gamma}_{\text{tot}}$ are averages of γ_{ij} taken respectively over the three nearest neighbors only and over all atom-pairs.

[37] L.M. Falicov and R.A. Harris, *J. Chem. Phys.* **51**, 3153 (1969).

[38] D. Denley and L.M. Falicov, *Phys. Rev B* **17**, 1289 (1978).

[39] G.F. Bertsch, A. Bulgac, D. Tomanek, Y. Wang, *Phys. Rev. Lett.* **67**, 2690 (1991).

[40] O. Gunnarsson and G. Zwicknagl, *Phys. Rev. Lett.* **69**, 957 (1992).

[41] J. Baker, P.W. Fowler, P. Lazzeretti, M. Malagoli and R. Zanasi, *Chem. Phys. Lett.* **184**, 182 (1991).

[42] From degenerate four-wave-mixing measurements in C₆₀-benzene solution, an unusually high absolute value of γ was inferred, $|\gamma| = 1.07 \times 10^{-28}$ esu (W.J. Blau, H.J. Byrne, D.J. Cardin, T.J. Dennis, J.P. Hare, H.W. Kroto, R. Taylor and D.R.M. Walton, *Phys. Rev. Lett.* **67**, 1423 (1991)). This value would lead to a third-order susceptibility in the *solid* two to three orders of magnitude larger than the one reported from other measurements. Critiques of this experiment showed that the measurements as well as the simple model used to explain this high value are questionable [R.J. Knize and J.P. Partanen, *Phys. Rev. Lett.* **68**, 2704 (1992) ; Z.H. Kalafi, F.J. Bartoli, J.R. Lindle, and R.G.S. Pong *Phys. Rev. Lett.* **68**, 2705 (1992)]. Therefore, this result is not considered here.

[43] See for instance P. Chopra, L. Carlucci, H.F. King, and P.N. Prasad, *J. Phys. Chem.* **93**, 7120 (1989) and references therein.

[44] K. Harigaya and S. Abe (Preprint 1992).

[45] After completion of this work the authors became aware of the results of a very similar study [L. Bergomi, J.P. Blaizot, Th. Jolicœur, and E. Dagotto, Preprint CE. Saclay SPhT/92-083], which shows also a transition between normal and SDW states at $\gamma_{ii} / \beta \approx 2.6$ in the Hartree-Fock approximation. In the present study the critical value is $\gamma_{ii} / \beta_1 \approx 2.82$ or equivalently $\gamma_{ii} / \beta_2 \approx 2.56$.

Table I. Two-center Coulomb integrals in benzene for first (γ_{12}), second (γ_{13}) and third (γ_{14}) nearest neighbors. The γ_{ij} are reported for $\gamma_{ii} = 10.72$ eV, as given in reference 29, and are expressed in eV.

γ_{12}	γ_{13}	γ_{14}
7.36 ^a	5.68 ^a	4.98 ^a
10.32 ^b	5.96 ^b	5.16 ^b
6.67 ^c	4.97 ^c	4.51 ^c
5.26 ^d	3.83 ^d	3.48 ^d
7.43 ^e	5.21 ^e	4.65 ^e

^a Best fit to the experimental energy levels for the exact solution of the PPP model [29].

^b Coulombic value.

^c Ooshika's [30] potential : $\gamma_{ij} = (e^2 / r_{ij}) [1 - \exp(-r_{ij}/R)]$, with $R = (e^2 / \gamma_{ii})$

^d Mataga-Nishimoto's [31] potential: $\gamma_{ij} = e^2 / (R + r_{ij})$ with $R = (e^2 / \gamma_{ii})$

^e Ohno's [32] potential : $\gamma_{ij} = e^2 / (R^2 + r_{ij}^2)^{1/2}$ with $R = (e^2 / \gamma_{ii})$

Table II. Values of the parameters of the PPP Hamiltonian and the geometrical parameters of C_{60} . The energies are expressed in eV, and the distances in Å.

β_2/β_1	β_2	γ_{ii}	r_1	r_2
1.1	2.5	11.13 ^a	1.45 ^b	1.40 ^b

^a For Section 4 only.

^b Experimental values of reference 33.

Table III . Comparison between experimental and calculated results for the linear optical properties of C₆₀. For all the experimental results, $\chi^{(1)}$ -- or a quantity directly related to it -- was measured (in the *solid*). For all the theoretical results, α is the quantity calculated for an *isolated molecule*. For the purpose of comparison, both α and $\chi^{(1)}$ are reported in all cases; the Clausius-Mossotti relation (11) is used for the conversion.

Type of Result	α (au)	$\chi^{(1)}$ (esu)	Measurement/Model	Reference
Experimental	569	0.24	refractive index	3
	621	0.29	EELS	4
	605	0.27	Capacitance	5
	530	0.21	ellipsometry	6
	569	0.24	NIR absorption	7
Theoretical	442.1	0.151	HF (6-31G* basis)	16
	557.9	0.229	LDA	17
	239.8	0.064	tight-binding	19
	288	0.081	conducting sphere	
	325.5	0.096	MP-2 ($\lambda=1$)	Present Calculation

EELS: Electron Energy-Loss Spectroscopy ;

NIR: Near Infra-red ;

LDA: Local Density Approximation.

Table IV. Details of the calculated values of the linear polarizability in C₆₀.

α (au)	Method	Reference
305.5	HF (STO-3G basis)	16
442.1	HF (6-31G* basis)	16
2099.7	LDA (bare)	17
557.9	LDA (screened)	17
1443.9	tight-binding (Hückel)	19
239.8	tight-binding (screened)	19
1168.9	Hückel	
318.9	FF, $\lambda=1$	Present
325.5	MP-2, $\lambda=1$	Calculation
387.8	SOS, $\lambda=1$	
252.5	FF, $\lambda=0$	
434.1	FF, $\lambda=2$	
379.7	FF, $\lambda=2$ (SDW)	

Table V . Experimental and calculated non-linear optical properties of C₆₀. The reported experimental values are $|\langle\gamma\rangle|$ for measurements in solution, and $|\chi_{1111}^{(3)}|$ for measurements on films. In reference 7 a ratio $\chi_{xyyx}^{(3)} / \chi_{xxxx}^{(3)}$ of (1/7) is found. The calculated quantity, except for reference 44, is γ in the static limit ($\omega = 0$); γ is found to be always positive. Calculations at finite frequency are also included in references 18 and 19. For the purpose of comparison, the connection between γ and $\chi^{(3)}$ is made using the Lorentz local-field correction of equation (12) and assuming a value of 2.0 for the refractive index.

Type of result	γ (10 ⁻³⁶ esu)	$\chi^{(3)}$ (10 ⁻¹² esu)	wavelength (μm)	Method (phase)	reference
Experimental	8.9 x 10 ³	2 x 10 ²	1.064	THG (film)	8
	3.1 x 10 ²	7	1.064	DFWM (film)	7
	7.5 x 10 ²	16.9	1.91	EISH (solution)	9
	10.3 x 10 ³	232	0.62	DFWM+OKG (solution)	18
	4.0 x 10 ²	9	1.9	THG (film)	9
	13.3 x 10 ²	30	1.32		
Theoretical	4.9	0.110	∞	INDO-TDCPHF	18
	2.3	0.052	∞	tight-binding	19
	/	1.22	∞	tight-binding ^a	44
Present	4.76	0.107	∞	$\lambda=1$, FF	
Calculation	5.87	0.132	∞	$\lambda=1$, MP-2	
	19.3	0.435	∞	$\lambda=1$, SOS	
	415.2	9.36	∞	Hückel	
	2.70	0.061	∞	$\lambda=0$, FF	
	12.6	0.284	∞	$\lambda=2$, FF	
	55.7	1.256	∞	$\lambda=2$, FF (SDW)	

THG: Third-Harmonic Generation ;

DFWM: Degenerate Four-Wave Mixing ;

EISH: Electric-Field Induced Second-Harmonic generation ;

OKG: Optical Kerr Gate.

^a In this approach both the enhancement by the Lorentz local field and the reduction caused by Coulomb interactions were neglected, with the assumption that they are mutually balanced.

FIGURE CAPTIONS

FIGURE 1. Expectation value of the local magnetic moment as a function of the on-site correlation, γ_{ii} , for various screening strengths. Dashed curve is for $\lambda = \infty$, full line is for $\lambda = 1$, and dashed-dotted line is for $\lambda = 0$.

FIGURE 2. Domains of stability of the SDW and CDW ground states for the PPP model on the C_{60} molecule. The vertical axis is the on-site Coulomb repulsion γ_{ii} and the horizontal axis is the screening strength, λ [see equation (13)]. The horizontal arrow indicates the asymptotic value for $\lambda \rightarrow \infty$ (*i.e.*, the Hubbard model).

FIGURE 3. Exploded view of the CDW ground state of the C_{60} molecule. Charge transfers indicated in the figure are for $\gamma_{ii} = 11.13$ eV and $\lambda=0$.

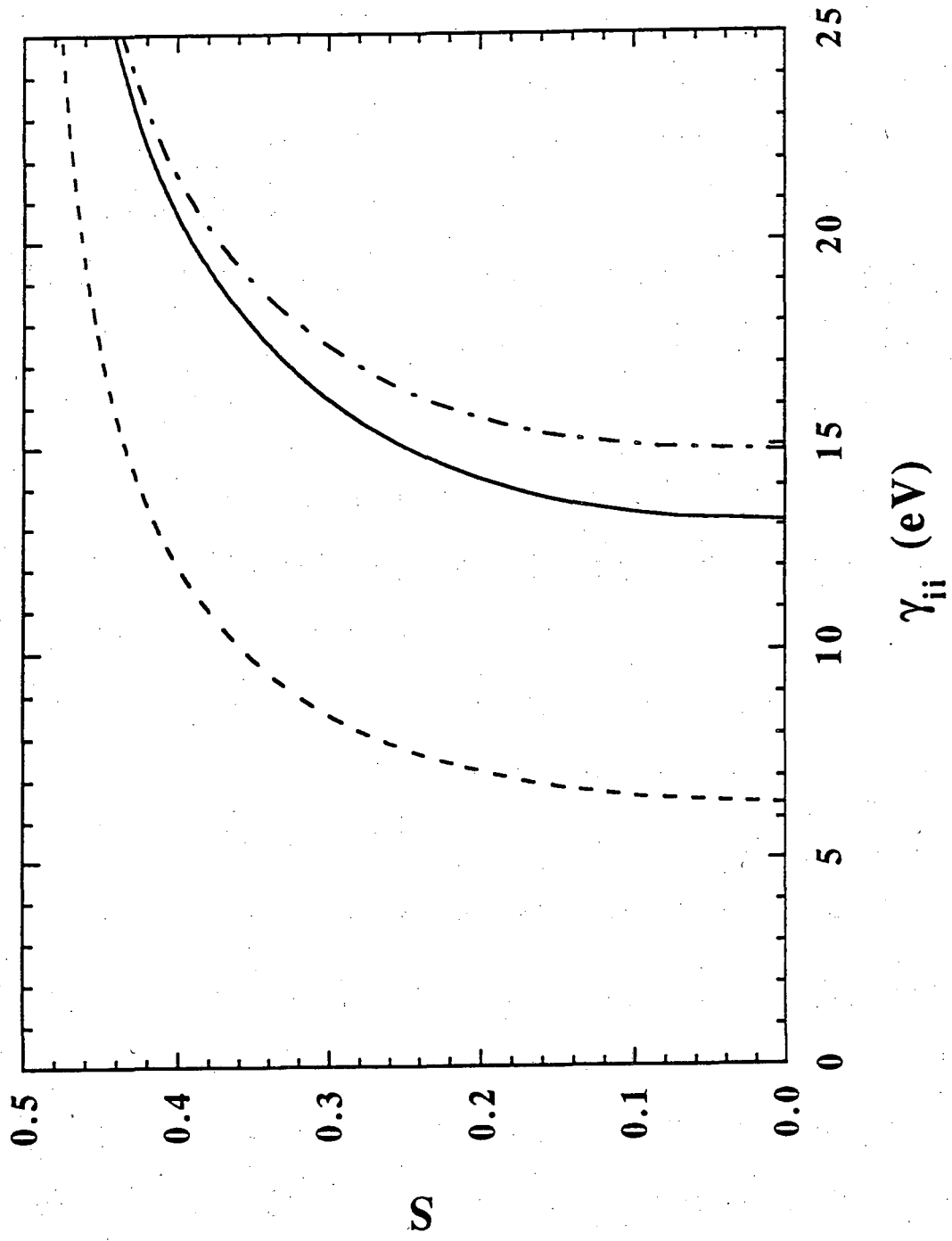


Figure 1

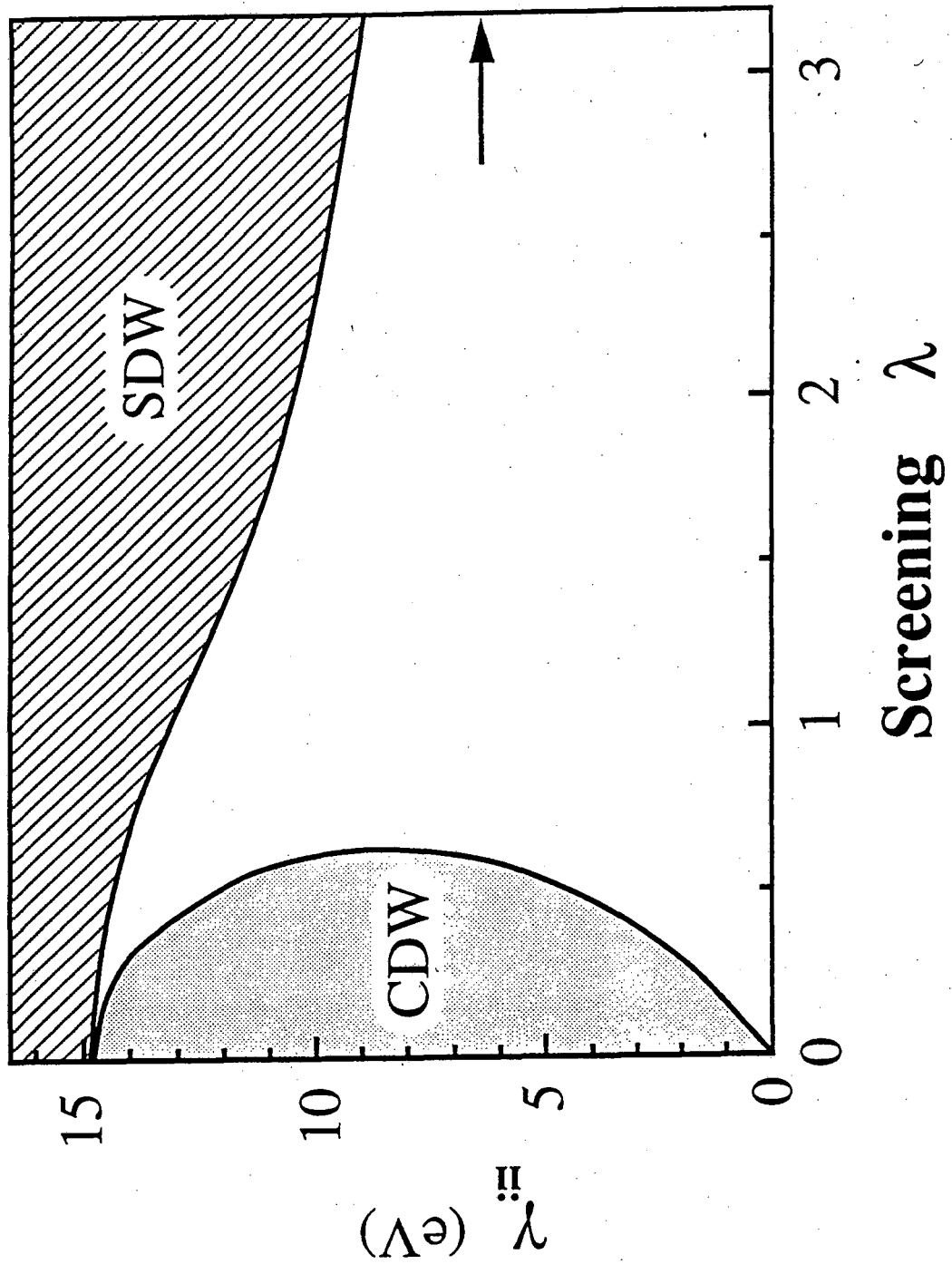


Figure 2

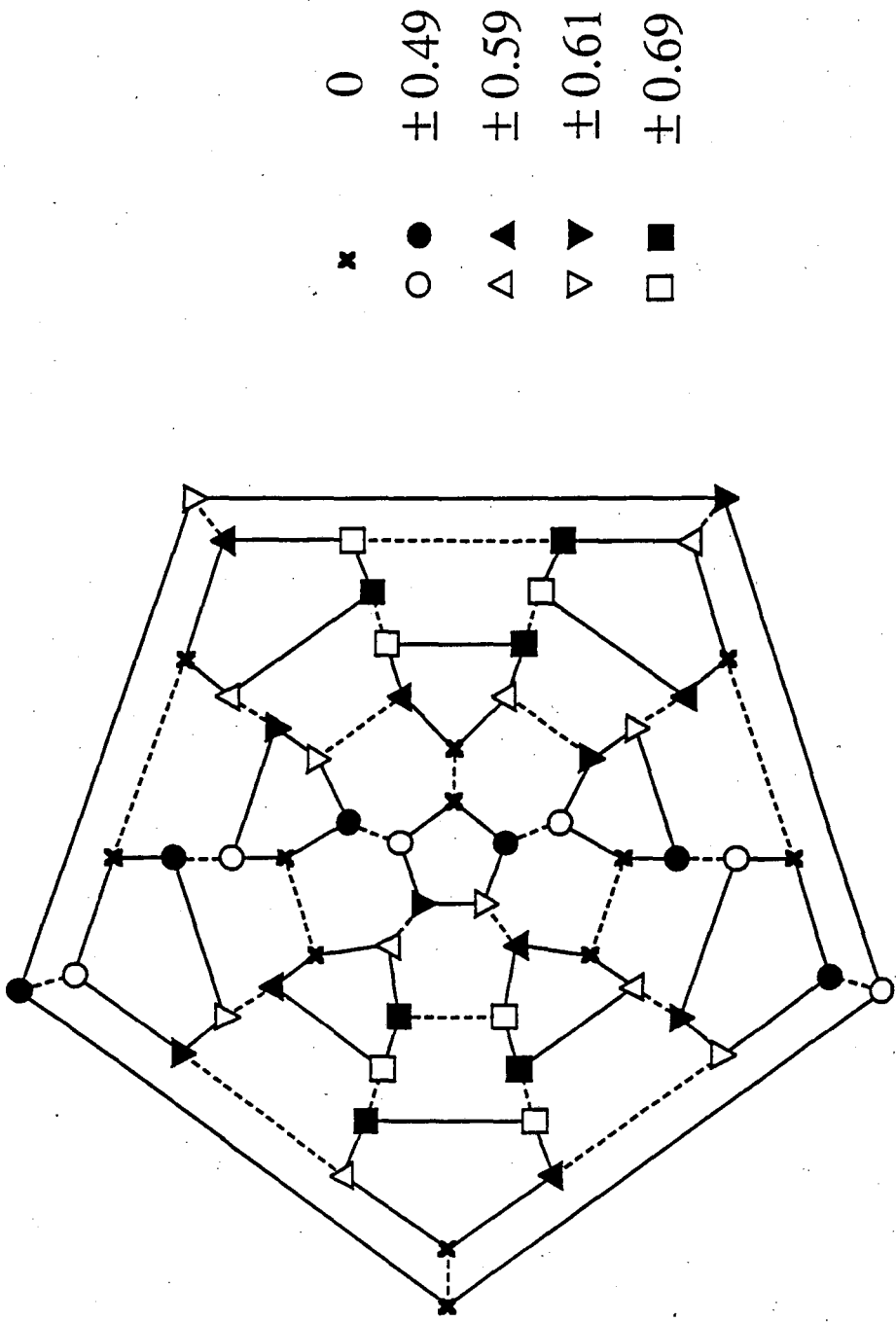


Figure 3

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720