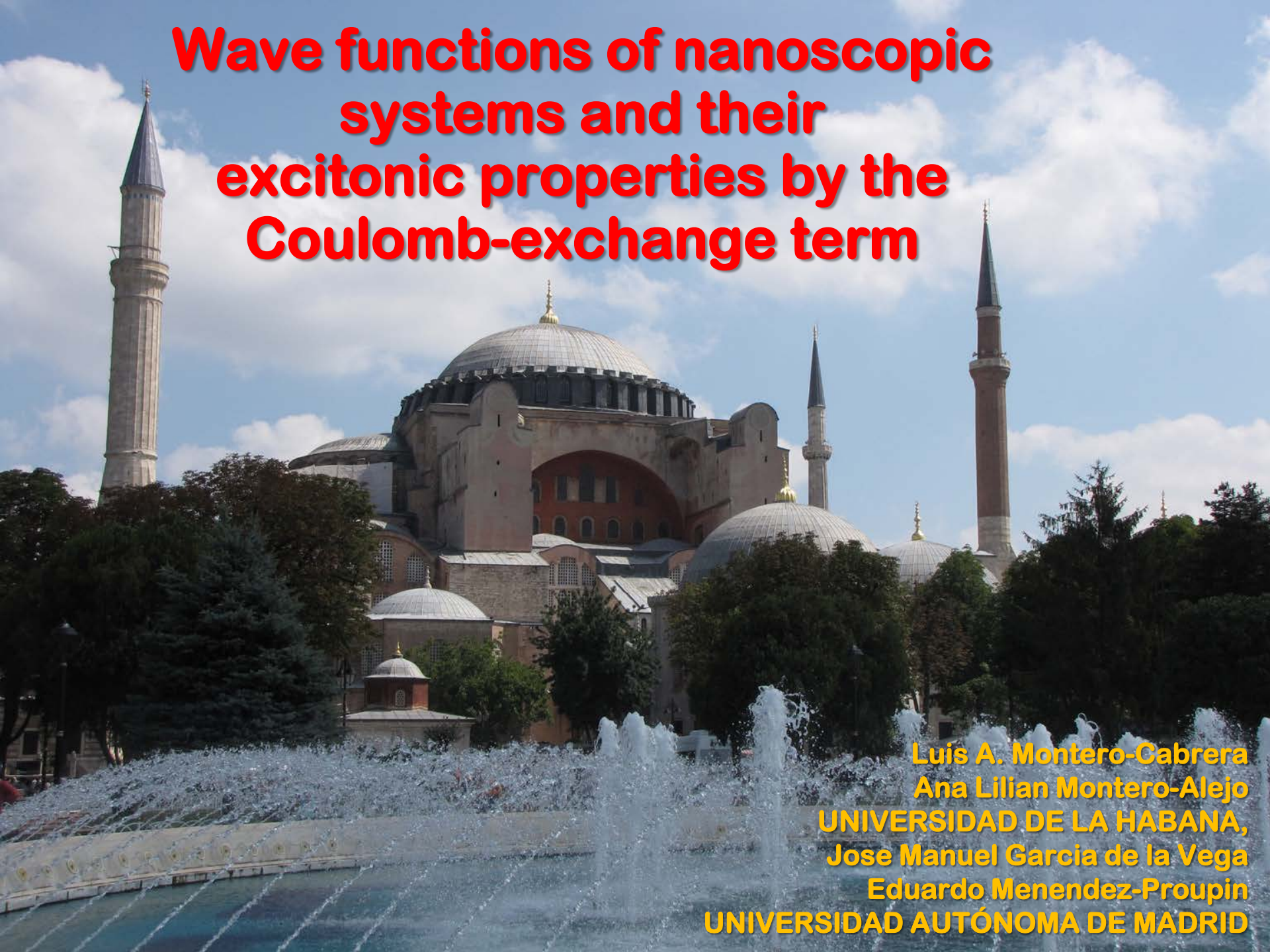


Wave functions of nanoscopic systems and their excitonic properties by the Coulomb-exchange term



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The problem

The structure and also the **electronic properties** of **nanoscopic systems** are real challenges for computational modeling because they are related with **key features of life and material sciences**.

The problem

Rigorously, **nanoscopic systems** are mostly suitable to be described by wave functions rather than classical routines because **electron exchange** and **charge density distributions** determine their behavior.

The problem

However, reaching a reliable **wave function** , even approximate, of a nanoscale system is a frequently **dismaying and very painful duty**.

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However, reaching a reliable **wave function** , even approximate, of a nanoscale system is a frequently dismaying and very painful duty.

Even harder is handling such wave function with **an appropriate Hamiltonian** to reach fine energies depending on their nuclei coordinates.



Nanoscopic systems are usually calculated and modeled as perfect crystals to take advantage of periodicity: calculating the unit cell allows a representation of the whole system

The problem

However, **modeling the collective capacity for exchanging energy with light and the consequent redistribution of charge across a nanoscopic geometry in different electronic states of non – periodic systems** appear now as essential to explain such phenomena and facilitate their applications.

Finding useful wave functions: Hartree – Fock procedures

Hartree – Fock's treatment

The Hartree – Fock's Hamiltonian considers electrons as navigating in the field of nuclei and uses antisymmetrized wave functions and Coulomb like potentials to account two kinds of electron interactions: electrostatic (J) and exchange (K).

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Operators of matrix elements are:

$$\hat{f}(r_m) = \hat{h}(r_m) + \sum_j \left(2\hat{J}_j(r_n) - \hat{K}_j(r_n) \right)$$

Hartree – Fock's treatment

Building and diagonalizing a Fock's matrix on reference "one electron" basis functions give **molecular orbitals** i.e. "one electron" energy state molecular functions:

$$\mathbf{F} = \begin{pmatrix} F_{11} & F_{12} & \dots & F_{1\mu} \\ F_{21} & F_{22} & \dots & F_{2\mu} \\ \vdots & \vdots & \dots & \vdots \\ F_{\nu 1} & \vdots & \dots & F_{\mu\mu} \end{pmatrix} \quad F_{\mu\nu} = h_{\mu\nu} + \sum_{\mu,\nu} \left[\sum_i n_i c_{\mu i} c_{\nu i} \right].$$

$$[2 \oint \chi_{\lambda}(r_m) \chi_{\mu}(r_n) \frac{1}{r_{mn}} \chi_{\nu}(r_m) \chi_{\sigma}(r_n) d\tau - \oint \chi_{\lambda}(r_m) \chi_{\mu}(r_n) \frac{1}{r_{mn}} \chi_{\sigma}(r_m) \chi_{\nu}(r_n) d\tau]$$

$$(\mathbf{F} - \mathbf{E}\mathbf{S})\mathbf{C} = 0$$

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$$(\mathbf{F} - \mathbf{E}\mathbf{S})\mathbf{C} = 0$$

This procedure is also followed for obtaining solutions within the so called Kohn-Sham's DFT.

Hartree – Fock's treatment

We must be aware that what we get in all cases are ϕ_i 's **one electron wave functions** of the complete system (as HOMO's and LUMO's are):

$$\phi_i = \chi c_i$$

Hartree – Fock's treatment

The common approach to understand *excitons* (charge – hole pair pseudoparticles) is after “exciting” electrons from filled i one electron states (HOMO's) to empty k one electron states (LUMO's).

Hartree – Fock's treatment

This approach has proven to be quite acceptable for filled levels, as comparisons between XPS ionizations and MO eigenfunctions show, but “excited” levels are rather uncertain

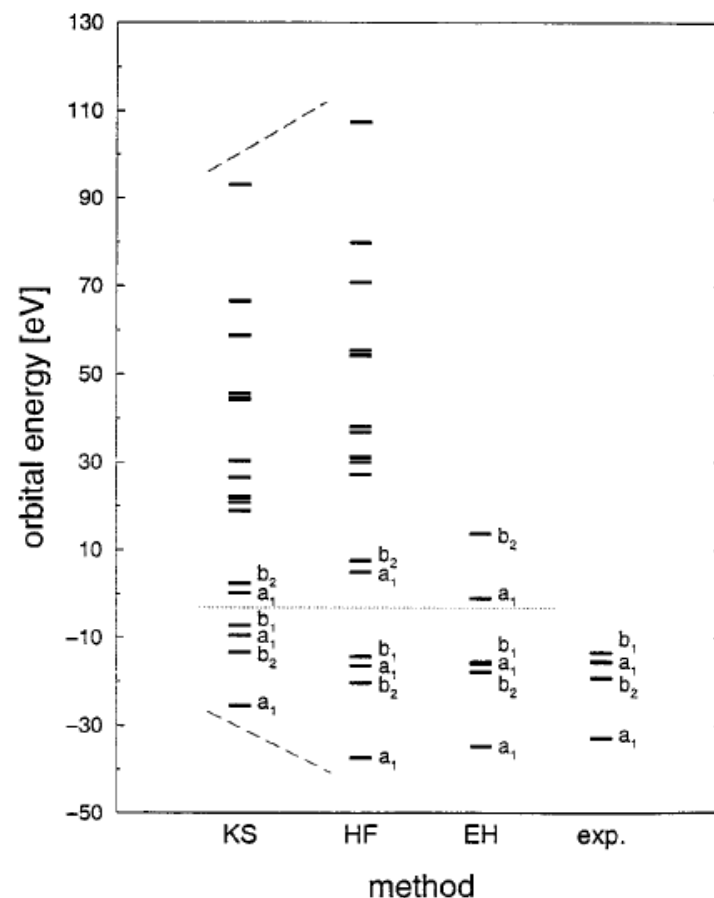


Figure 1. Calculated occupied valence and virtual orbitals for water by BP86/6-31G*, RHF/6-31G*, and eH methods, as well as the experimental values.³⁹ The Fermi level is indicated by a dotted line; the compression of the KS levels relative to HF levels is highlighted by dashed lines.

Stowasser, R.; Hoffmann, R., What Do the Kohn–Sham Orbitals and Eigenvalues Mean? J. Am. Chem. Soc. 1999, 121 (14), 3414-3420.

Computational modeling of electron excitations

Modeling electron excitation properties of polyatomic systems has been an important goal since the very beginnings of the application of quantum mechanics to chemistry.

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Modeling electron excitation properties of polyatomic systems has been an important goal since the very beginnings of the application of quantum mechanics to chemistry.

Molecular mechanical procedures can model nothing in this respect .

Computational modeling of electron excitations

Two considerations must be accomplished regarding the theoretical methods:

- Seeking to obtain numerical results of electron excitation energies and charge displacements comparable to experiments as the main goal

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Two considerations must be accomplished regarding the theoretical methods:

- Seeking to obtain numerical results of electron excitation energies and charge displacements comparable to experiments as the main goal
- Preserving theoretical coherence to reach reliable models of molecular excitations to allow understanding and prediction of physical processes.

Computational modeling of electron excitations

- *A priori* methods are better for understanding and modeling because they are depending more on the ground theory than on selected parameters.

Computational modeling of electron excitations

- *A priori* methods are better for understanding and modeling because they are depending more on the ground theory than on selected parameters.
- *A posteriori* methods are good for numerical predictions because they use known values in benchmark molecules to adjust Hamiltonians and give numerical results.

CNDOL: A reliable “a priori”, approximate Hamiltonian

1. Montero-Cabrera, L. A.; Röhrig, U.; Padron-García, J. A.; Crespo-Otero, R.; Montero-Alejo, A. L.; García de la Vega, J. M.; Chergui, M.; Röthlisberger, U., CNDOL: A fast and reliable method for the calculation of electronic properties of very large systems. Applications to retinal binding pocket in rhodopsin and gas phase porphine. *J. Chem. Phys.* **2007**, *127* (14), 145102.
2. Montero, L. A.; Alfonso, L.; Alvarez, J. R.; Perez, E., From PPP-MO theory to all-valence electron calculations of ionic and excited states in organic molecules. *Int. J. Quantum Chem.* **1990**, *37* (4), 465-83.

The NDOL Formalism

Translated to an atomic basis, the NDOL formalism is an approximate Hartree-Fock's procedure for calculations of energy and composition of valence molecular orbitals:

$$F_{\mu\mu} = H_{\mu\mu} + \sum_{A \neq B} \left(P_B^l \gamma_{AB}^{ll} + P_B^k \gamma_{AB}^{lk} \right)$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} p_{\mu\nu} \gamma_{AB}^{lk}$$

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$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} p_{\mu\nu} \gamma_{AB}^{lk}$$

All terms are “a priori” evaluated and provide consistent and reliable results

The NDOL Formalism

Our method takes into account the basic approximations to build **a genuine Hartree – Fock Hamiltonian** with implicit basis functions and a frozen atomic core for lighter elements.

The NDOL Formalism

Description and proposed nomenclature for the CNDOL/1 diagonal one - electron matrix elements $(H_{\mu\mu})^a$.

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} V_{AB}^l$$

CNDO origin	$U_{\mu\mu}$	$\sum_{B \neq A} V_{AB}^l$	
		$-\sum_{B \neq A} (Z_B^l \gamma_{AB}^{ll} + Z_B^k \gamma_{AB}^{lk})$ Split core charge: S	$-\sum_{B \neq A} Z_B \Gamma_{AB}^l$ Complete core charge: C
CNDO/1	$-I_\mu + \gamma_{AA}^{ll} - Z_A^l \gamma_{AA}^{ll} - Z_A^k \gamma_{AA}^{lk}$ Split core charge: 1S	CNDOL/1SS	CNDOL/1SC
	$-I_\mu + \gamma_{AA}^{ll} - Z_A \gamma_{AA}^{ll}$ Complete core charge: 1C	CNDOL/1CS	CNDOL/1CC

a. I_μ and A_μ are the valence state ionization potential and electron affinity, respectively, of the AO μ ; Z is the effective nuclear charge of the atomic core; Γ_{AB}^l is the interaction integral between an electron with azimuthal quantum number l on atom A with the core of atom B. CNDOL/1SS and CNDOL/1CC correspond with the previous names CNDOL/11 and CNDOL/12, respectively.

The NDOL Formalism

Description and proposed nomenclature for the CNDOL/2 diagonal one - electron matrix elements $(H_{\mu\mu})^a$.

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} V_{AB}^l$$

CNDO origin	$U_{\mu\mu}$	$\sum_{B \neq A} V_{AB}^l$	
		$-\sum_{B \neq A} (Z_B^l \gamma_{AB}^{ll} + Z_B^k \gamma_{AB}^{lk})$ Split core charge: S	$-\sum_{B \neq A} Z_B \Gamma_{AB}^l$ Complete core charge: C
CNDO/2	$-\frac{1}{2}(I_\mu + A_\mu) + \frac{1}{2}\gamma_{AA}^{ll} - Z_A^l \gamma_{AA}^{ll} - Z_A^k \gamma_{AA}^{lk}$ Split core charge: 1S	CNDOL/2SS	CNDOL/2SC
	$-\frac{1}{2}(I_\mu + A_\mu) + \frac{1}{2}\gamma_{AA}^{ll} - Z_A \gamma_{AA}^{ll}$ Complete core charge: 1C	CNDOL/2CS	CNDOL/2CC

a. I_μ and A_μ are the valence state ionization potential and electron affinity, respectively, of the AO μ ; Z is the effective nuclear charge of the atomic core; Γ_{AB}^l is the interaction integral between an electron with azimuthal quantum number l on atom A with the core of atom B. CNDOL/2SS and CNDOL/2CC correspond with the previous names CNDOL/21 and CNDOL/22, respectively.

The NDOL Formalism

While one center off diagonal elements are neglected, two center terms appear for all options as:

$$H_{\mu\nu} = -\frac{1}{2}(I_{\mu} + I_{\nu})f(r_{\mu\nu}, l_{\mu}, l_{\nu}, q_{\mu\nu})$$

being the projection term:

$$f(r_{\mu\nu}, l_{\mu}, l_{\nu}, q_{\mu\nu}) = S_{\mu\nu} f'(q_{\mu\nu})$$

The NDOL Formalism: term evaluation

Two electron integrals on a single center A are evaluated by means of the Pariser's relation :

$$\gamma_{AA}^{ll} = I_{\mu} - A_{\mu}$$

The NDOL Formalism: term evaluation

A general formula has been used for two center – two electron integrals:

$$\gamma_{AB}^{lk} = \left(a_{AB}^{lk\ 2} + cR_{AB}a_{AB}^{lk} + R_{AB}^2 \right)^{-1/2}$$

that becomes the Mataga – Nishimoto's when $c = 2$, Ohno's when $c = 0$, and the so called “modified Ohno's” when $c = 1$.

The NDOL Formalism: term evaluation

The total energy is:

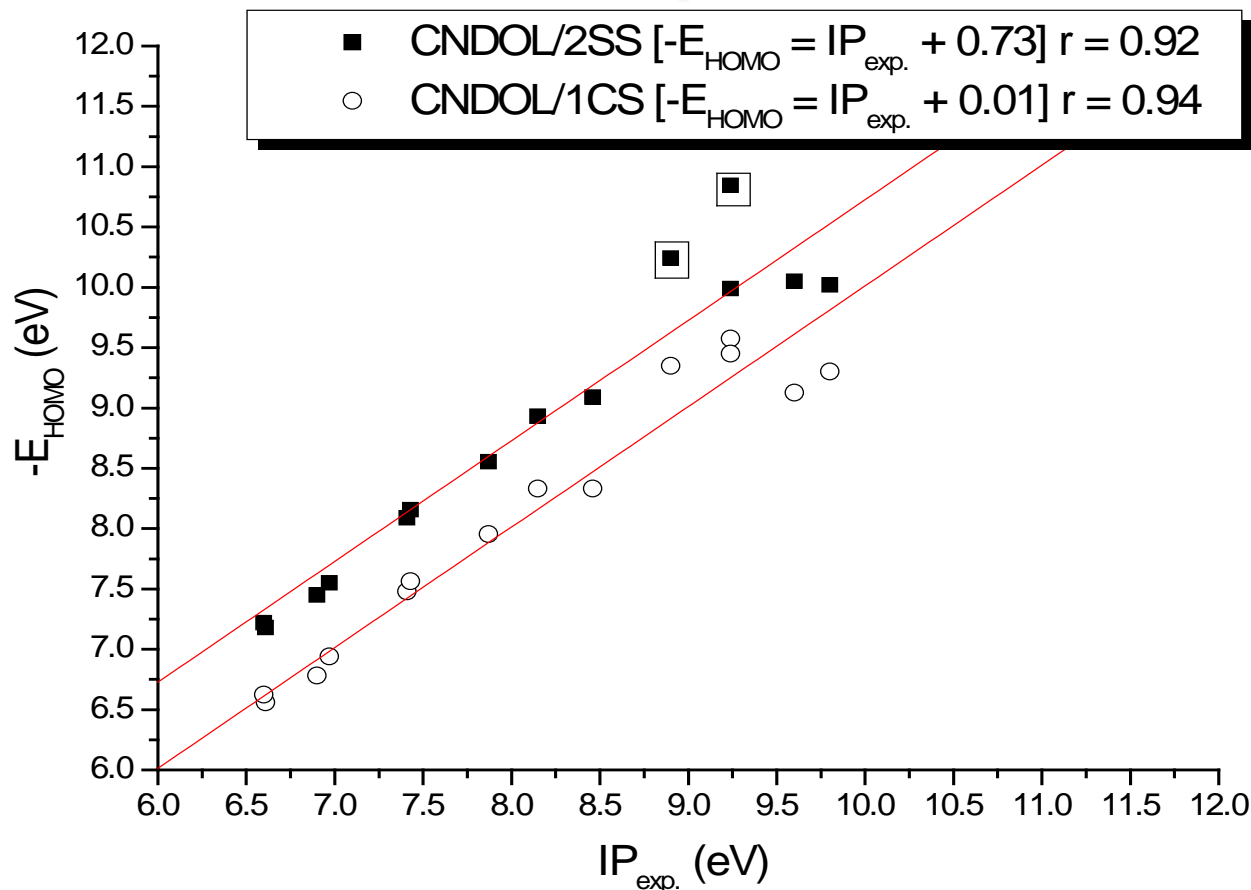
$$E = \sum_{\mu \leq \nu} p_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) + \sum_{A < B} Z_A Z_B R_{AB}^{-1}$$

“A priori” character confirmed

Only I_μ , A_μ and **Slater exponents** for calculating $S_{\mu\nu}$ are basis parameters, and they are always taken from data published elsewhere.

**How reliable are these
molecular wave functions?**

CNDOL HOMO's vs. molecular ionization potentials



Linear regression between the experimental ionization potentials ($IP_{exp.}$) of a molecule set and the corresponding module of the HOMO energies obtained by the CNDOL/2SS (filled square) and CNDOL/1CS (open circle) SCF procedure, imposing a unitary slope.

**Excited states from singly
excited configuration
interaction**

Configuration interaction of singles (CIS)

Each ζ excited state can be obtained from a variational procedure, well known as “configuration interaction” (CI):

$$\Psi_{\zeta}^{CIS} = \sum_{\sigma} a_{\sigma M} \Phi_{\sigma}$$

$$(\mathbf{H} - \mathbf{E})\mathbf{a} = 0$$

where \mathbf{E} is a diagonal matrix of their excited state eigenvalues.

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where \mathbf{E} is a diagonal matrix of their excited state eigenvalues.

They all correspond to each optimized multi-electronic wave function Ψ_{ζ}^{CIS} .

Configuration interaction of singles (CIS)

The SCF transition energies:

$${}^1H_{\sigma\sigma} = \varepsilon_{j^*} - \varepsilon_i - J_{ij^*} + 2K_{ij^*}$$

$${}^3H_{\sigma\sigma} = \varepsilon_{j^*} - \varepsilon_i - J_{ij^*}$$

are used as diagonal elements* in the single excitation CI matrix (ε_i and ε_{j^*} are molecular orbital eigenvalues of occupied and unoccupied levels, respectively)

* Non diagonal elements are only made by up to four center two electron integrals.

One electron MO's vs. CIS for electronic transitions

MO view

Based on one electron states (MO's) resulting from SCF or other iterative energy optimizations. **Virtual states are not optimized because density elements of matrix have no value for them.** Believable OMO's, uncertain UMO's.

One electron MO's vs. CIS for electronic transitions

MO view

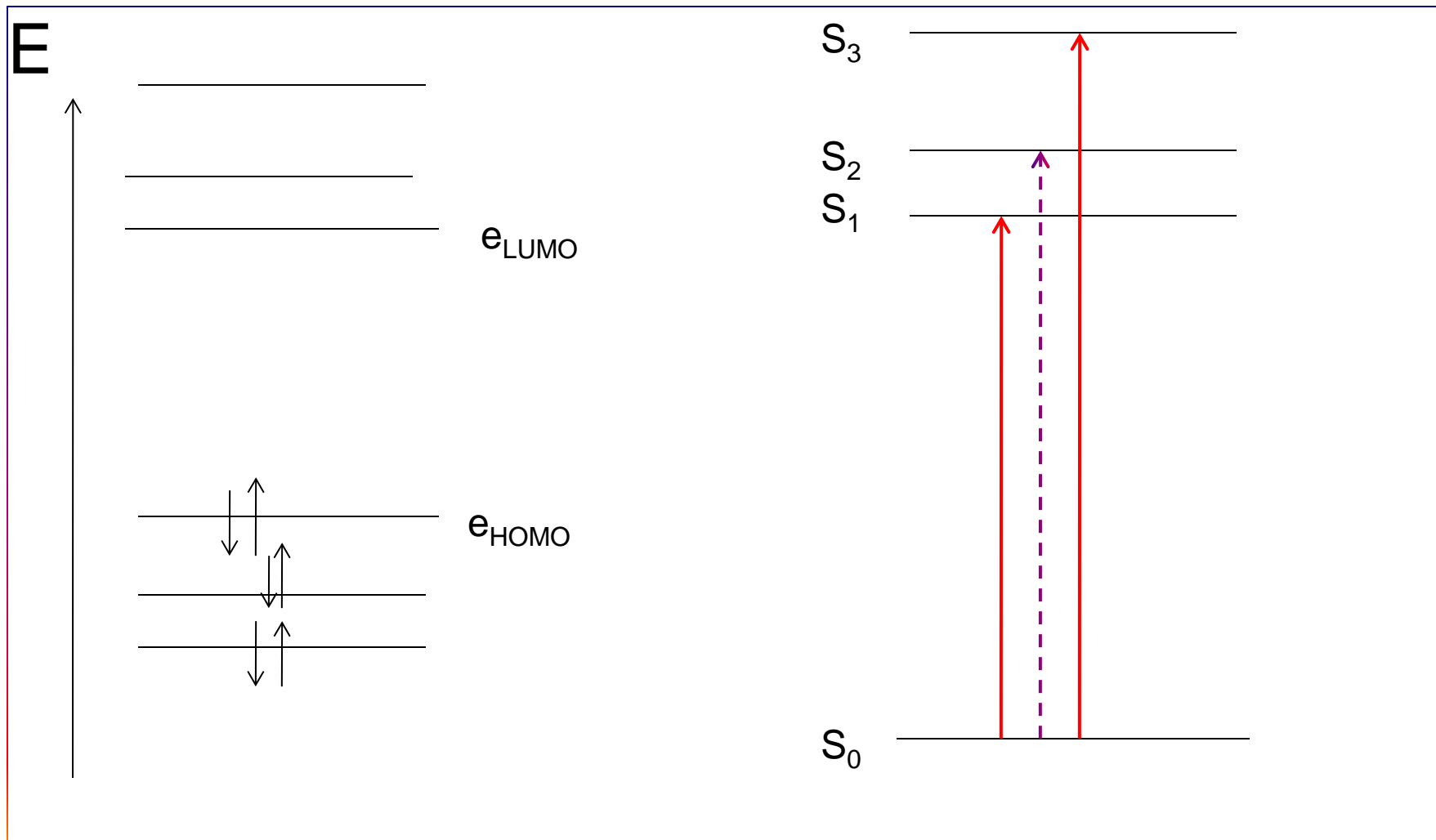
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Believable OMO's, uncertain UMO's.

CIS view

Resulting from a variational optimization of every state above the fundamental, and accounting both Coulombic and exchange interactions between every electron pair *in the molecule*.

One electron MO's vs. CIS for electronic transitions



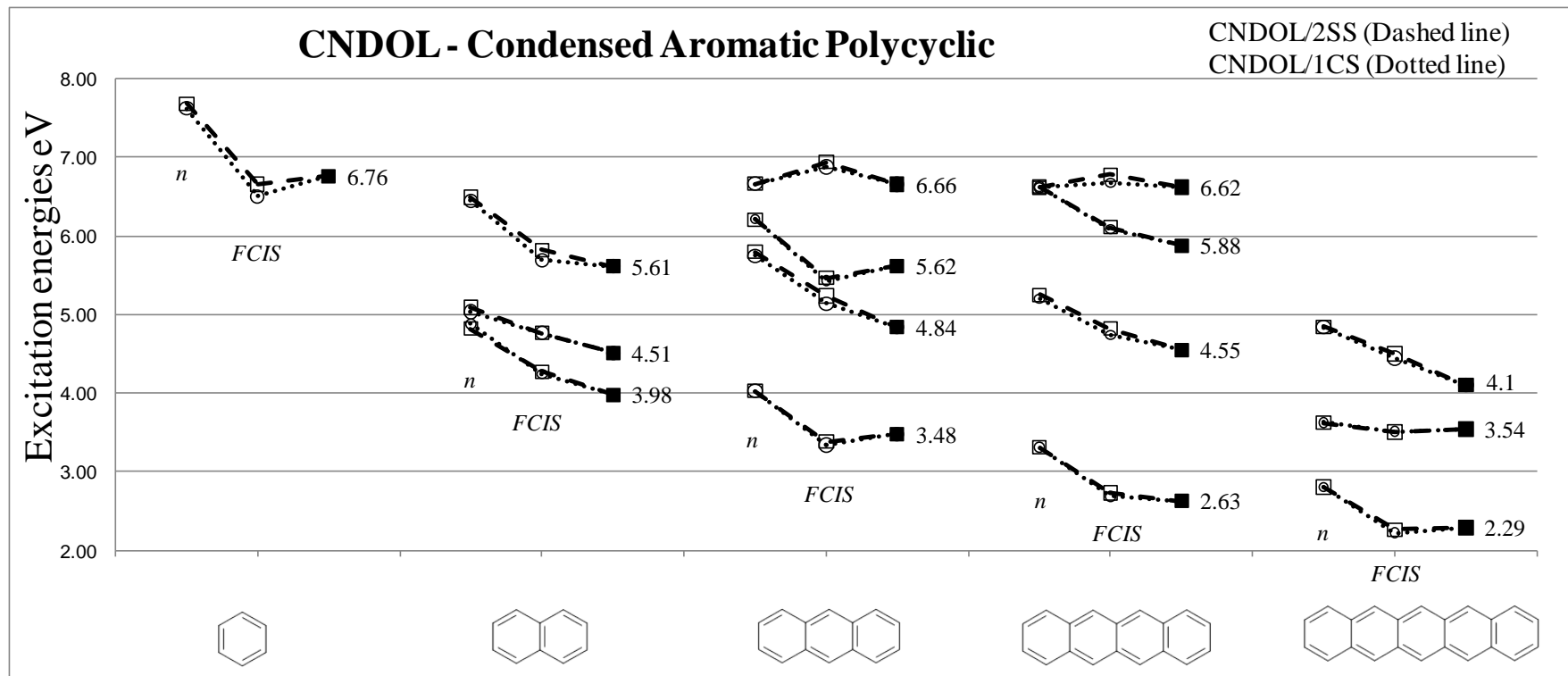
In our procedure all possible SCF single transition energies are evaluated and ordered according to their increasing values.

CIS matrix is then built with the σ lowest energy terms of such singly excited determinants, where σ is chosen by a procedure based on the appearance of “bands”, and then diagonalized.

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Benchmarking Full CIS



CNDOL/2SS (solid line) and CNDOL/1CS (dotted line) excitation energies for a set of aromatic condensed-polycyclic hydrocarbons. The experimental maxima of the absorption spectra in hydrocarbon solution (marked as filled) were used as reference data.

Excited state electron densities

Electron density terms of each σ **singly excited configuration** comes from SCF matrices:

$$p_{\mu\nu}^{\sigma} = \sum_{i=1}^N n_i^{\sigma} c_{i\mu} c_{i\nu}$$

where n_i^{σ} is the occupation number of each i MO in the σ state (being $n_i^{\sigma} = 0, 1, 2$ according to the number of electrons in each MO corresponding to the σ determinant) and $c_{i\mu}$ are the MO coefficients.

Excited state electron densities

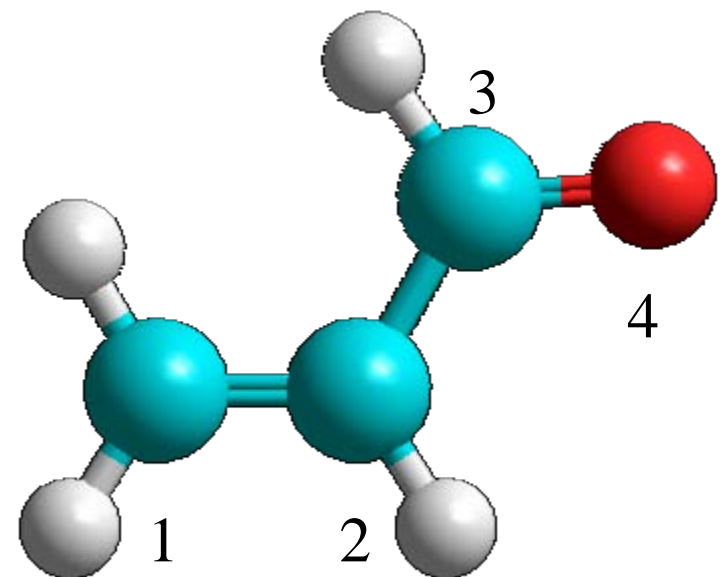
Then, **density elements of each ζ CI state** is given by the squares of the corresponding coefficients and densities of SCF excited states:

$$p_{\mu\nu}^{\zeta} = \sum_{\sigma=1}^M a_{\sigma\zeta}^2 p_{\mu\nu}^{\sigma}$$

Modeling the physical meaning of an electron excitation

When $p_{\mu\nu}^{\zeta}$ is calculated and known, the physical meaning of each ζ electron excitations becomes evident as a charge reorganization corresponding to each excited state with respect to the ground state.

Charge displacements upon excitation of acrolein (CNDOL/2CC full CIS)



The calculated photochemical behavior points to the approach and reaction of a C1 that becomes negative charged upon excitation to a non excited monomer showing a positive charge at the equivalent site

S1($n\pi^*$)

S0

	Q_{O4}	$\Delta Q_{O4}(p)$	ΔQ_{O4}	Q_{C1}	$\Delta Q_{C1}(p)$	ΔQ_{C1}	Q_{C2}
S1($n\pi^*$)	-0.511	0.296	0.296	-0.226	-0.363	-0.364	0.109
S0	-0.807			0.138			0.102

Excitons and configuration interaction

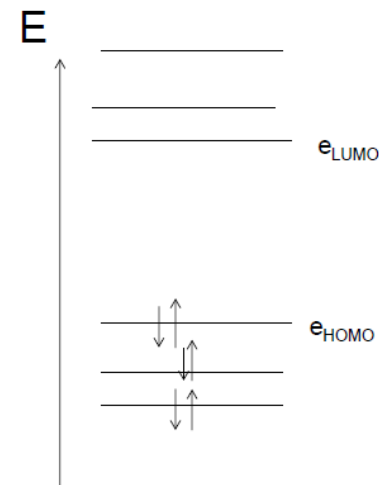
The concept of exciton in the one electron wave function representation is a “charge – hole” pair quasi-particle which energy is related with **charge binding** between the corresponding excited and ground states.

Excitons and configuration interaction

Coulomb and exchange terms are both geometry and charge distribution dependent effects modifying differences between one electron state eigenvalues.

$${}^1H_{\sigma\sigma} = \varepsilon_{j^*} - \varepsilon_i - J_{ij^*} + 2K_{ij^*}$$

$${}^3H_{\sigma\sigma} = \varepsilon_{j^*} - \varepsilon_i - J_{ij^*}$$



Excitons and configuration interaction

The Coulomb – exchange terms express the energy of charge migrations occurring upon excitation, and how they remain loose or tight to the original ground state density distribution:

$${}^1E_{CE} = -J_{ij^*} + 2K_{ij^*}$$

$${}^3E_{CE} = -J_{ij^*}$$

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$${}^3E_{CE} = -J_{ij^*}$$

Therefore, the total value of MO Coulombic (J 's) and exchange (K 's) integrals *could be considered as related with the binding between electrons and their left empty one - electron states (holes) in the case of single determinant excitations.*

Excitons and configuration interaction

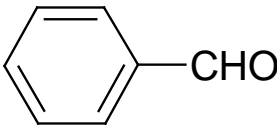
Therefore, Coulomb-Exchange terms for each multielectronic excited state will be:

$${}^1E_{\zeta}^{CE} = \sum_{\sigma=1}^M a_{\sigma\zeta}^2 \left(-J_{ij^*} + 2K_{ij^*} \right)_{\sigma}$$

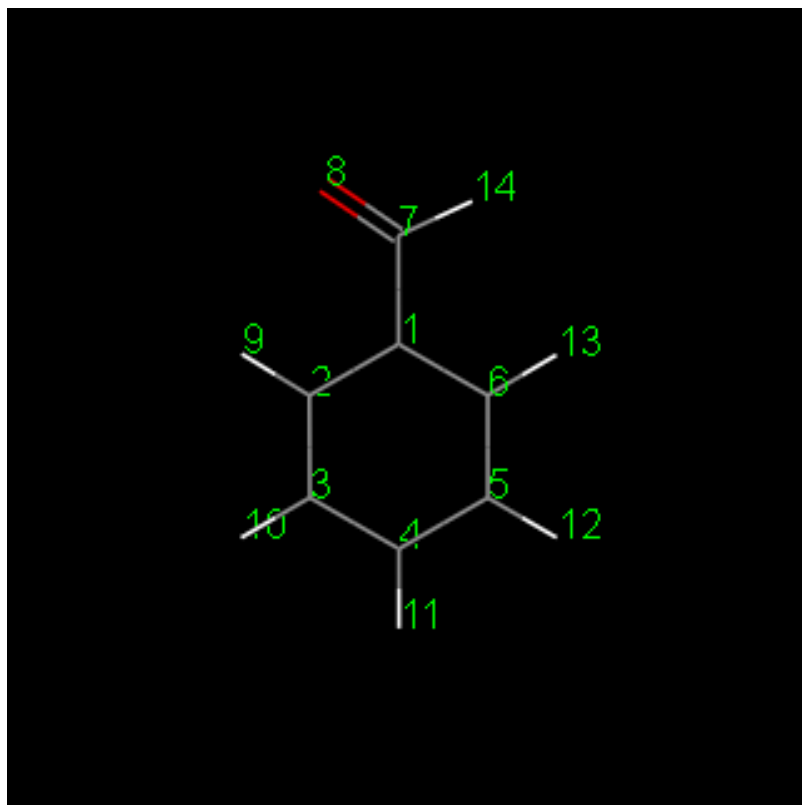
$${}^3E_{\zeta}^{CE} = \sum_{\sigma=1}^M a_{\sigma\zeta}^2 \left(-J_{ij^*} \right)_{\sigma}$$

It could be considered as related with the *exciton charge binding* energy after CIS.

Coulomb – exchange terms in benzaldehyde


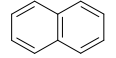
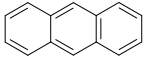
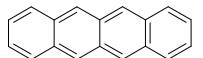
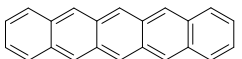
Coulomb – exchange energies ($^1E^{CE}$) in eV obtained by tested CNDOL theoretical approaches.				
Molecules		State s	$^1E^{CE}$ (eV)	
			CNDOL/2SS	CNDOL/1CS
Benzaldehyde		$n-\pi^*$	4.98	5.17
		$\pi-\pi^*$	5.34	5.18
		$\pi-\pi^*$	3.66	3.67
		$\pi-\pi^*$	3.83	4.01

Coulomb – exchange terms in benzaldehyde (CNDOL/1CS)



E^{CE} (ev)	5.17	5.18	3.67	4.01
Atom	ΔQ	ΔQ	ΔQ	ΔQ
C1	0.0525	0.0518	0.0140	-0.0159
C2	-0.0249	0.0793	0.0078	0.0694
C3	0.0097	-0.0027	-0.0161	0.0539
C4	-0.0035	-0.1104	-0.0476	-0.0539
C5	-0.0047	-0.0011	-0.0023	0.0526
C6	-0.0226	0.0455	0.0091	0.0642
C7	-0.1149	-0.1744	-0.1349	-0.1917
O8	-0.0858	0.0061	0.0603	-0.0191
H9	0.0515	0.0044	0.0145	0.0068
H10	0.0418	0.0189	0.0136	0.0086
H11	0.0034	0.0277	0.0199	0.0068
H12	0.0552	0.0074	0.0155	0.0073
H13	0.0361	0.0114	0.0173	0.0070
H14	0.0060	0.0362	0.0289	0.0039

Coulomb – exchange terms of polyacenes

Molecule	Structural formula	Origin	CNDOL/2SS	CNDOL/1CS
Benzene		$\pi-\pi^*$	3.91	3.96
Naphthalene		$\pi-\pi^*$	3.33	3.34
		$\pi-\pi^*$	3.63	3.64
		$\pi-\pi^*$	3.69	3.73
Anthracene		$\pi-\pi^*$	2.91	2.92
		$\pi-\pi^*$	3.33	3.36
		$\pi-\pi^*$	3.51	3.51
		$\pi-\pi^*$	3.52	3.49
Naphthacene		$\pi-\pi^*$	2.62	2.63
		$\pi-\pi^*$	3.09	3.10
		$\pi-\pi^*$	3.08	3.08
		$\pi-\pi^*$	3.13	3.14
Pentacene		$\pi-\pi^*$	2.40	2.41
		$\pi-\pi^*$	2.90	2.90
		$\pi-\pi^*$	2.76	2.76

The case of benzene clusters

Benzene aggregates can illustrate how Coulomb - exchange term behaves and serve for.

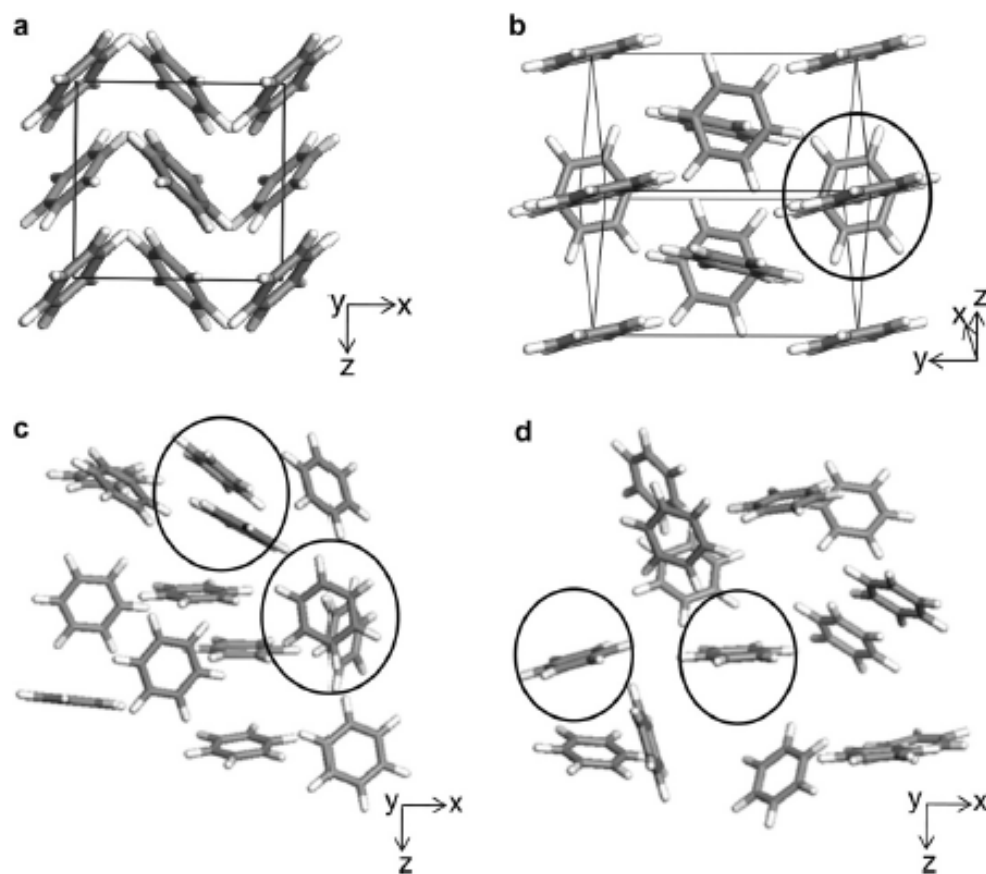


Figure 4. Benzene aggregate models. Panels (a) and (b) show herringbone structures of the unit cell crystalline solid benzene at different orientations. Panels (c) and (d) show two typical structures of the liquid models with different conformations among all interacting benzenes and with isolated molecules into the aggregate, respectively.

The case of benzene clusters

Excitons in crystals and “ordered liquids” are loose, although homogeneous.

Liquids show varied behaviors.

Non interacting benzene molecules show again tight excitons because they are local in each ring. However, orbital differences are very large.

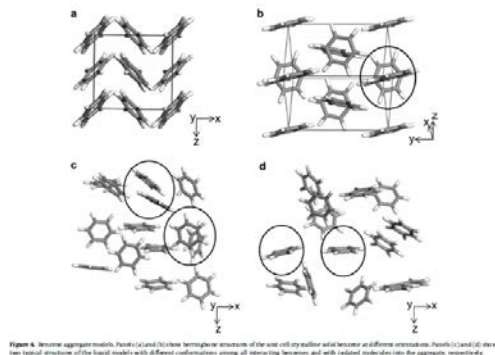


Figure 4. Schematic aggregate models. Panels (a) and (b) show herringbone structures of the real crystal with different orientations. Panels (c) and (d) show the typical structure of the liquid model with different conformations among interacting molecules and with related molecules in the aggregate, respectively.

$$^1H_{\zeta\zeta} = (\varepsilon_{j^*} - \varepsilon_i) - (J_{ij^*} + 2K_{ij^*})$$

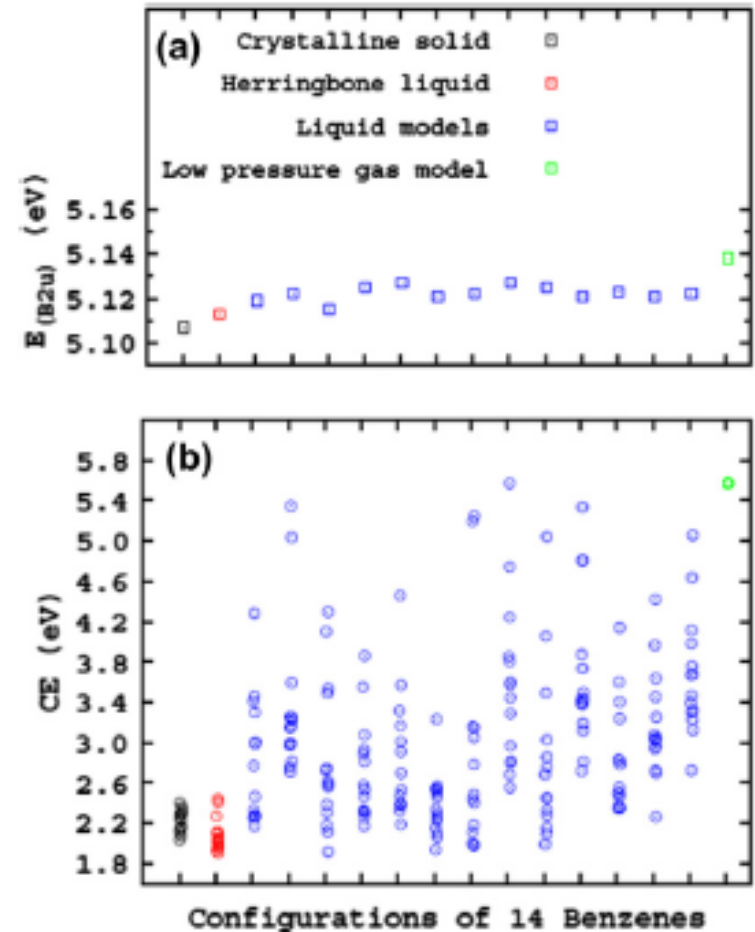
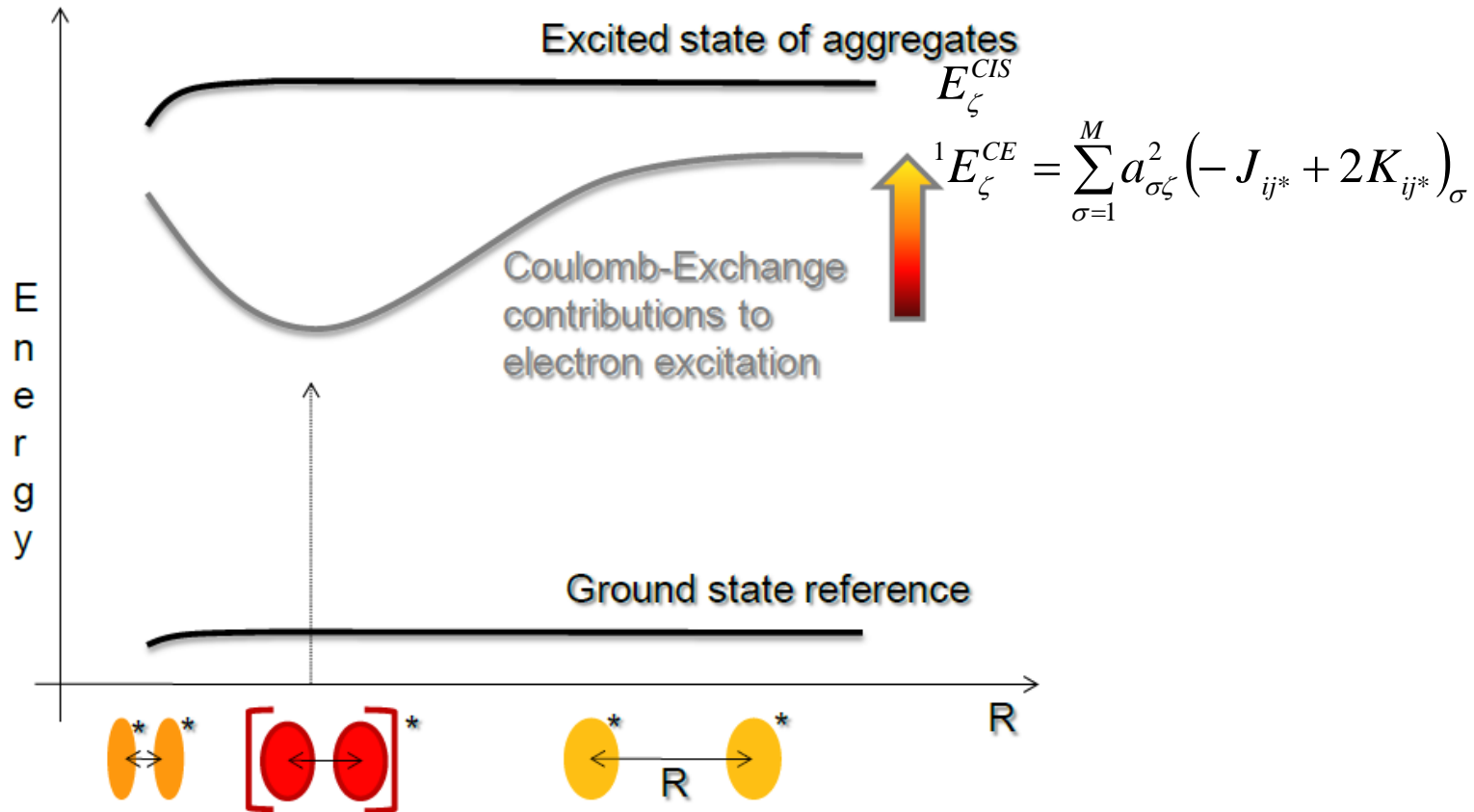


Figure 5. Dotted squares of panel (a) correspond to the energies of the first singlet excited states of different conformations of 14 benzene molecules: crystalline solid in black, herringbone liquid in red, uncorrelated liquid models in blue and the low pressure gas model in green. Dotted circles in panel (b) show CE contributions to the corresponding low-energy excitations of each conformation (colors are in correspondence to the labels in panel (a)).

The case of benzene clusters



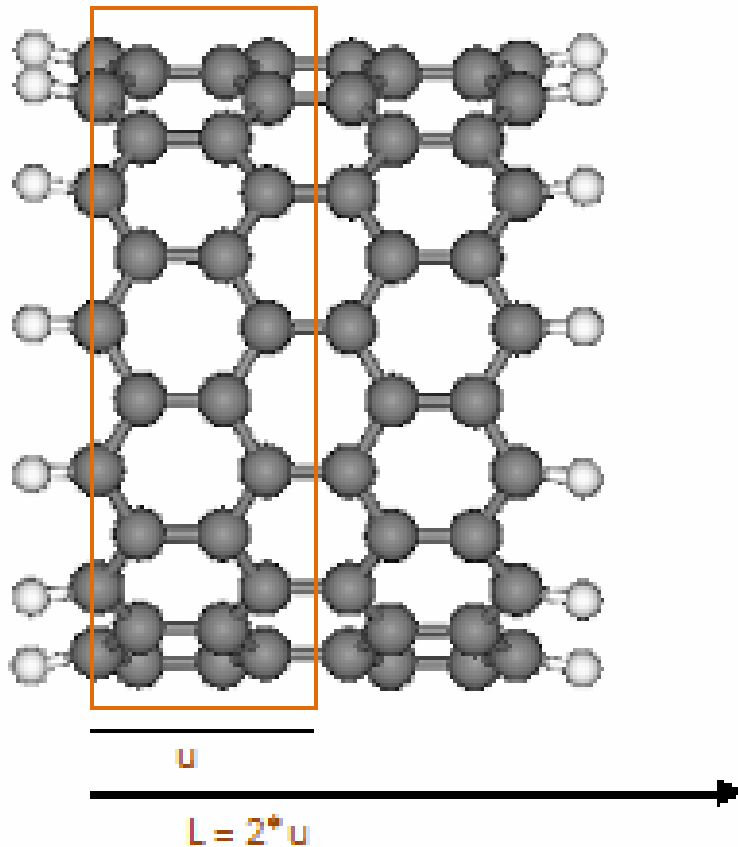
Some applications to excited states of polyatomic systems



Nanotubes

Montero-Alejo, A. L.; Fuentes, M. E.; Menéndez-Proupin, E.; Orellana, W.; Bunge, C. F.; Montero, L. A.; García de la Vega, J. M., Approximate quantum mechanical method for describing excitations and related properties of finite single-walled carbon nanotubes. *Phys. Rev. B* **2010**, **81** (23), 235409.

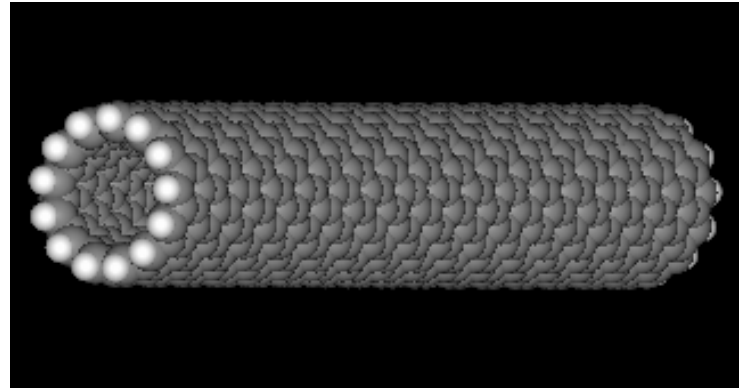
Models of Single-Walled Carbon Nanotubes (SWCNT)



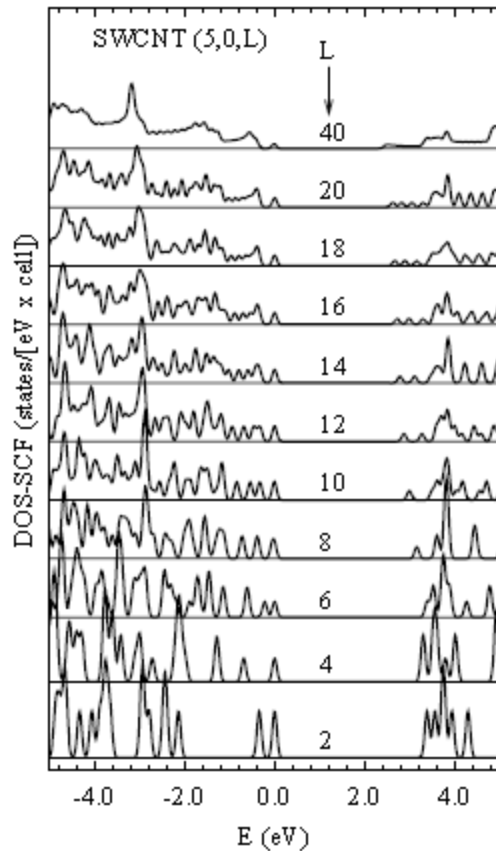
Zig-zag type SWCNT,
within $(n-m=3M)$ rule

L	Length (nm)
2	0.71
4	1.56
6	2.42
8	3.27
10	4.12
12	4.98
14	5.83
16	6.68
18	7.54
20	8.39

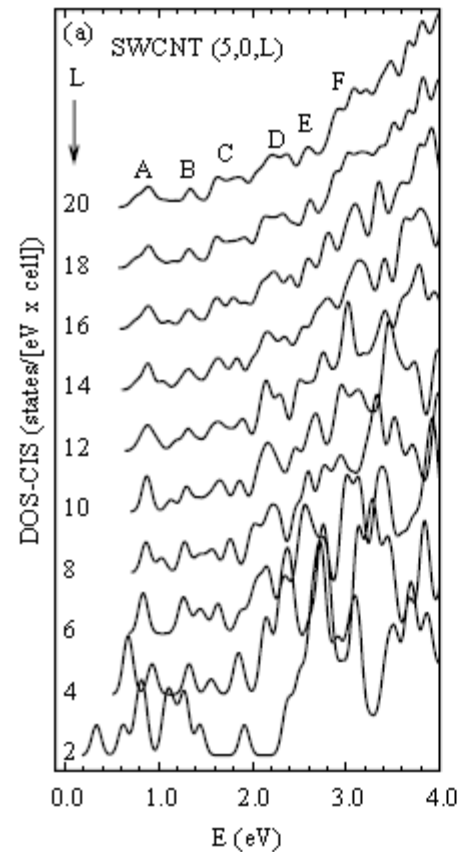
SWCNT(13,0,16)



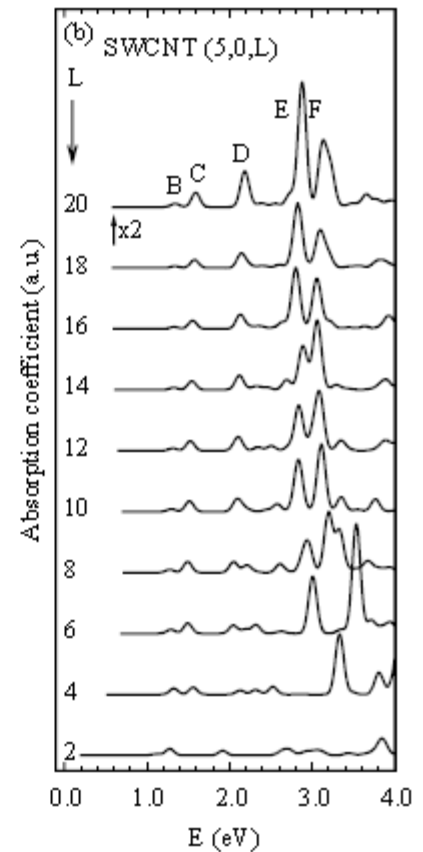
Two visions of the same phenomenon



MO-DOS
(one electron wave functions)

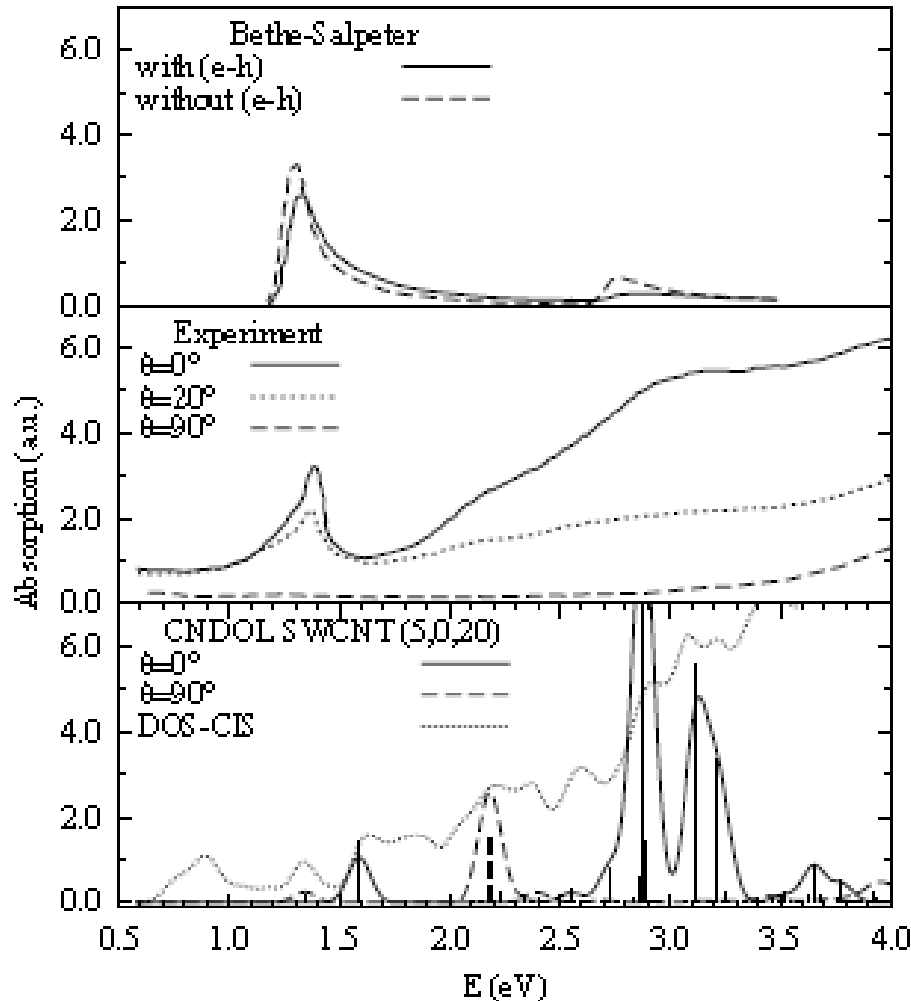


CIS-DOS



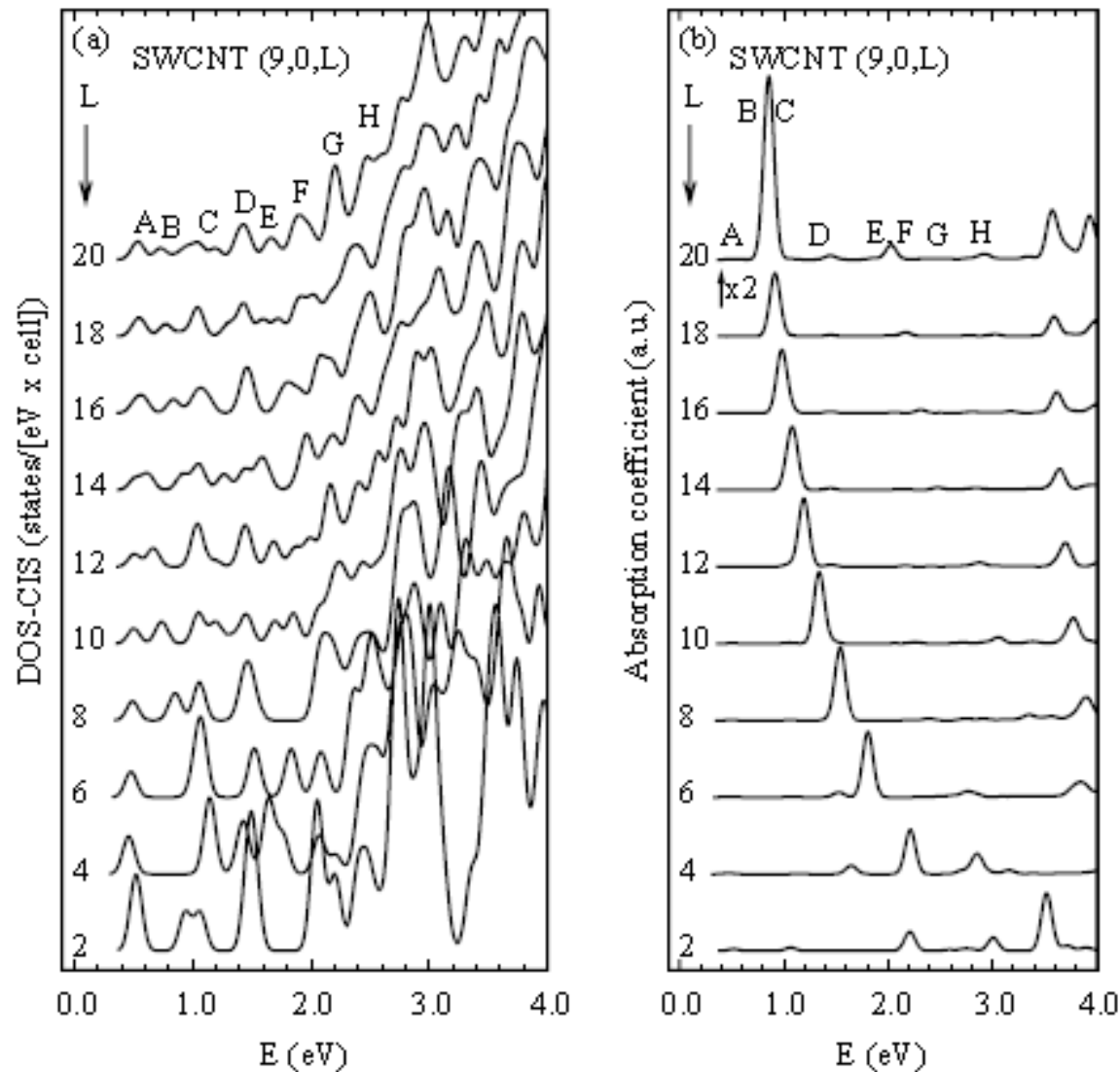
Calculated
transition energies
(all electron wave functions)

Experiment vs. theory for (5,0,20) SWCNT

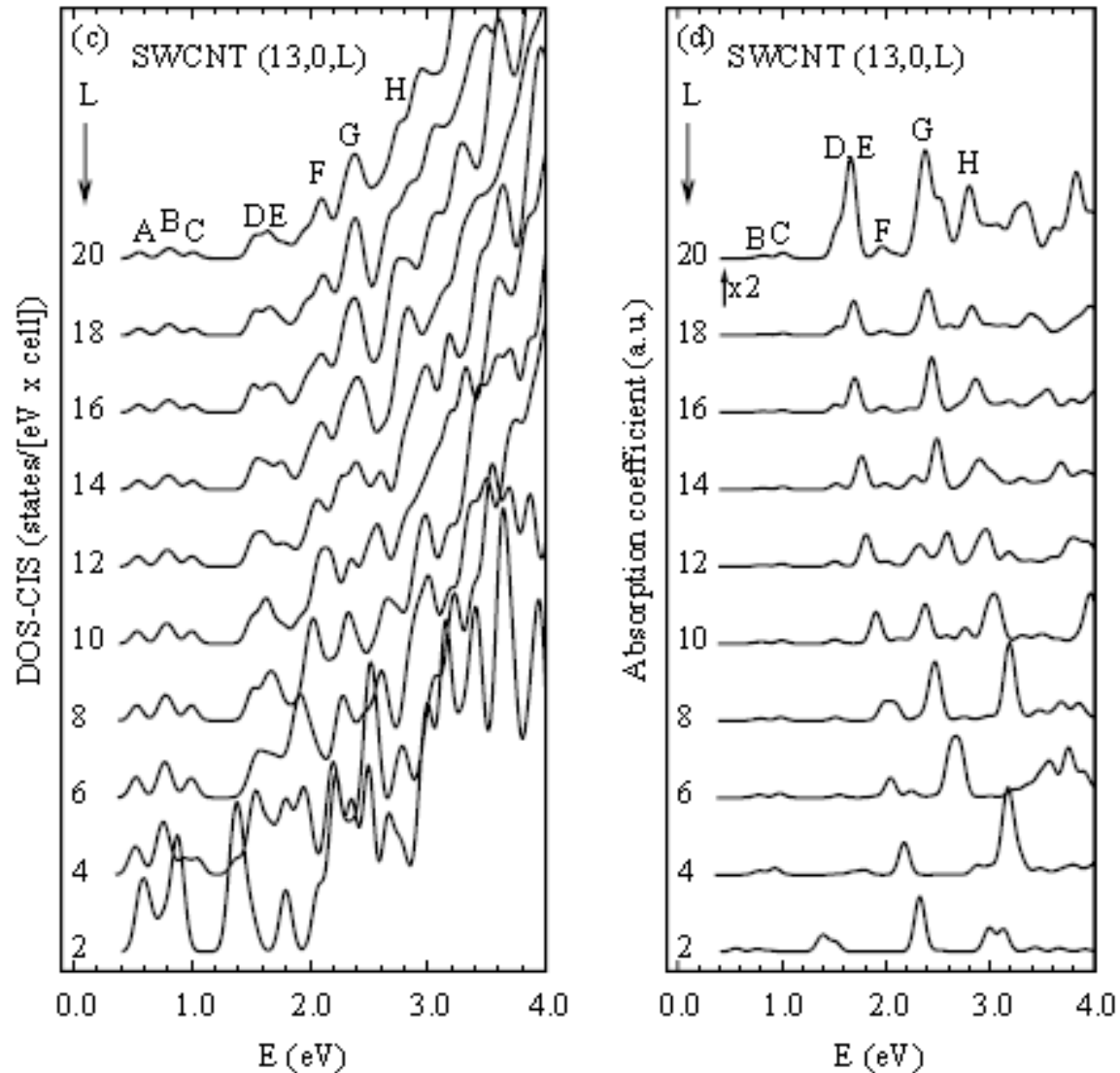


Middle, experimental optical absorption spectra of SWCNT with diameter near 4 Å located in the pores of a zeolite. Top, calculated imaginary part of the dielectric function, obtained with the Bethe-Salpeter equation. Bottom, CNDOL absorption spectrum of (5,0,20) SWCNT. The electric field of light is polarized along the nanotube axis.

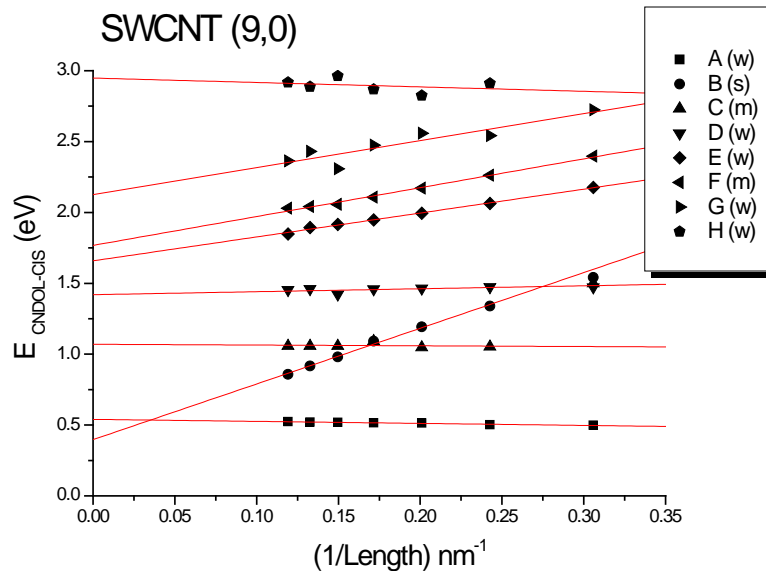
The case of (9,0) SWCNT



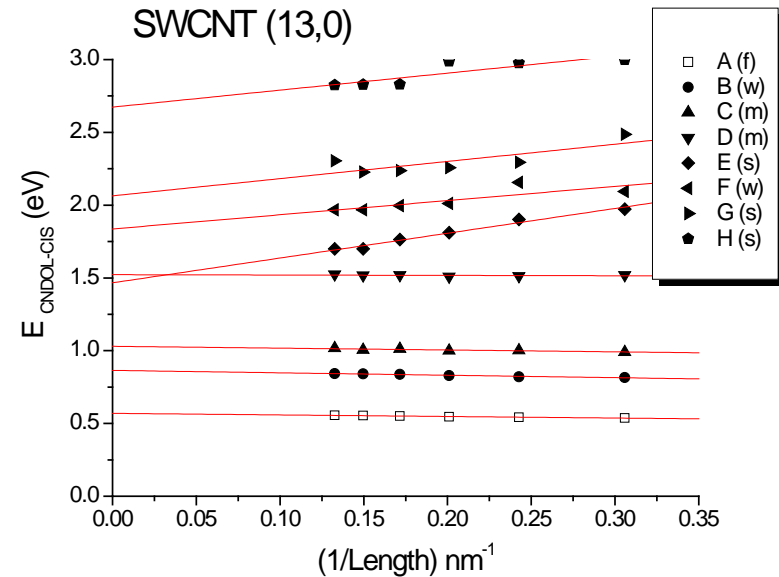
The case of (13,0) SWCNT



How they evolve when projected to infinite lengths?



When length tend to infinite the lowest excited state of (9,0) SWCNT converges to about 0.4 eV



When length tend to infinite the lowest excited state of (13,0) SWCNT remains unchanged and forbidden for direct light absorption around 0.6 eV

Fullerene clusters

Montero-Alejo, A. L.; Menendez-Proupin, E.; Fuentes, M. E.; Delgado, A.; Montforts, F. P.; Montero-Cabrera, L. A.; Garcia de la Vega, J. M., Electronic excitations of C₆₀ aggregates. *PCCP* **2012**, *14* (37), 13058-13066.

Modeling C_{60} aggregates

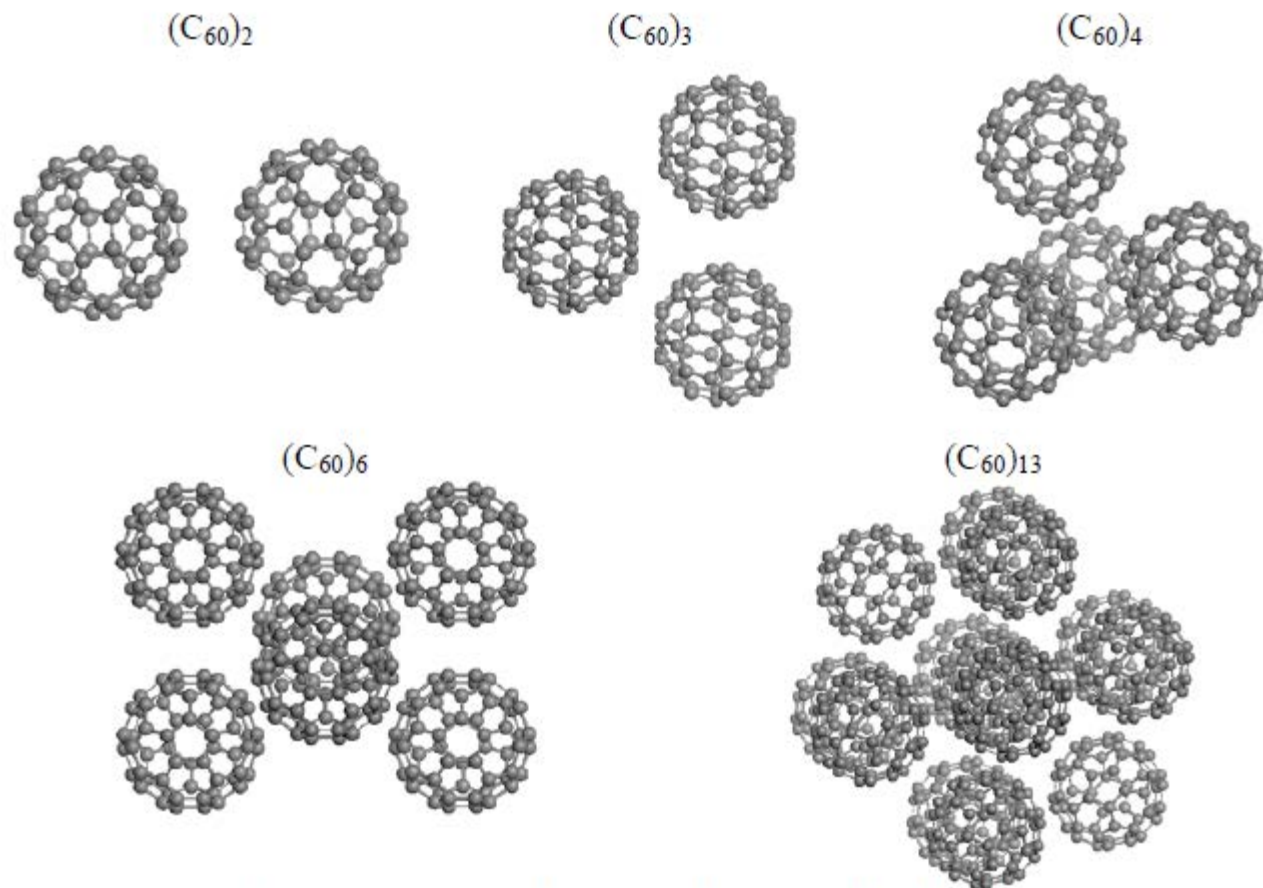


FIG. 1. Structural arrangements of the $(C_{60})_N$ cluster models. The distance between neighboring C_{60} molecules (fullerene center-center) in the crystal is 10.02 Å.

Modeling C₆₀ aggregates

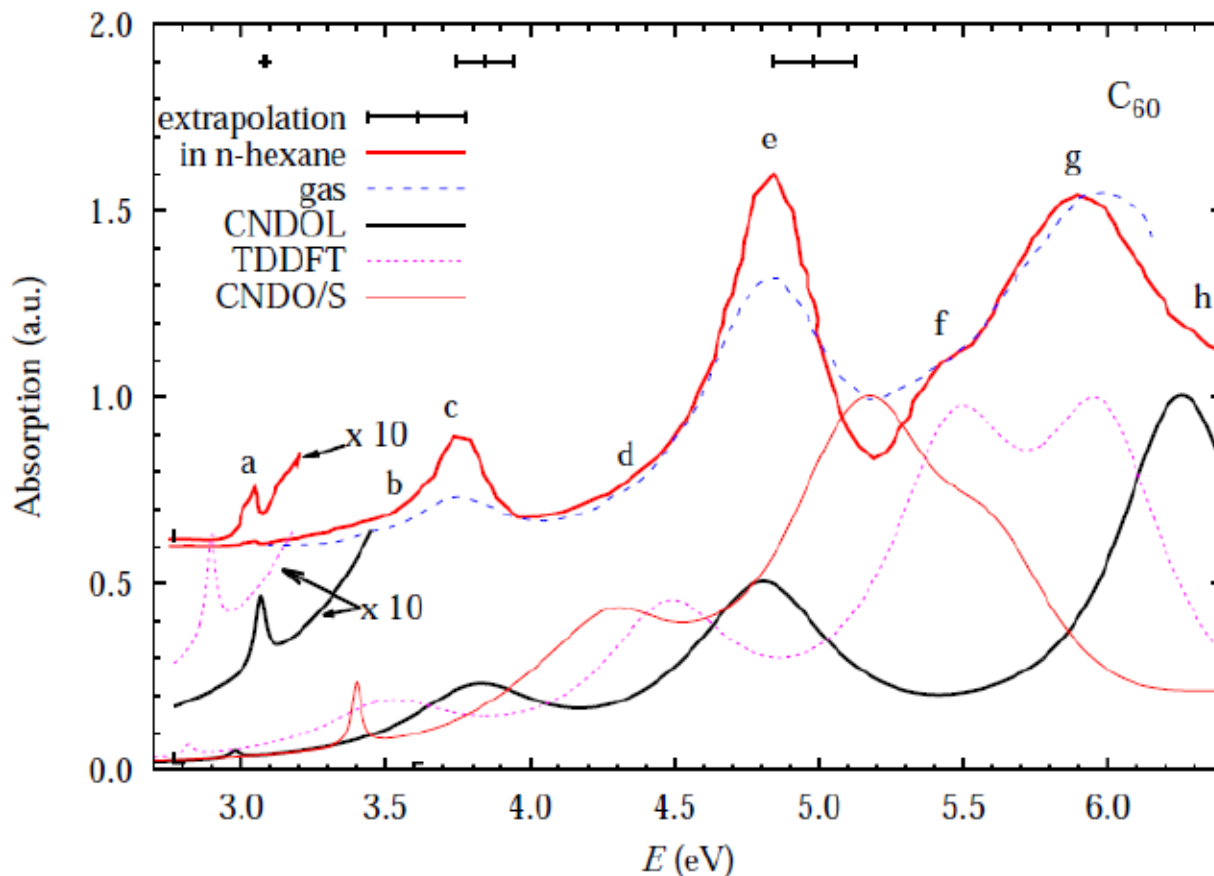


FIG. 2. (Color online) Experimental and theoretical absorption spectra of C₆₀. The experimental values are reported in *n*-hexane solution at 300 K⁷ and from a molecular beam at an estimated temperature 973 K.⁹ Calculations are made with CNDOL (this work), TDDFT,²¹ and CNDO/S²⁴ methods. Horizontal error bars represent the extrapolated peak energies and bandwidths as estimated for a cold gas phase spectrum.¹⁰

Modeling C_{60} aggregates

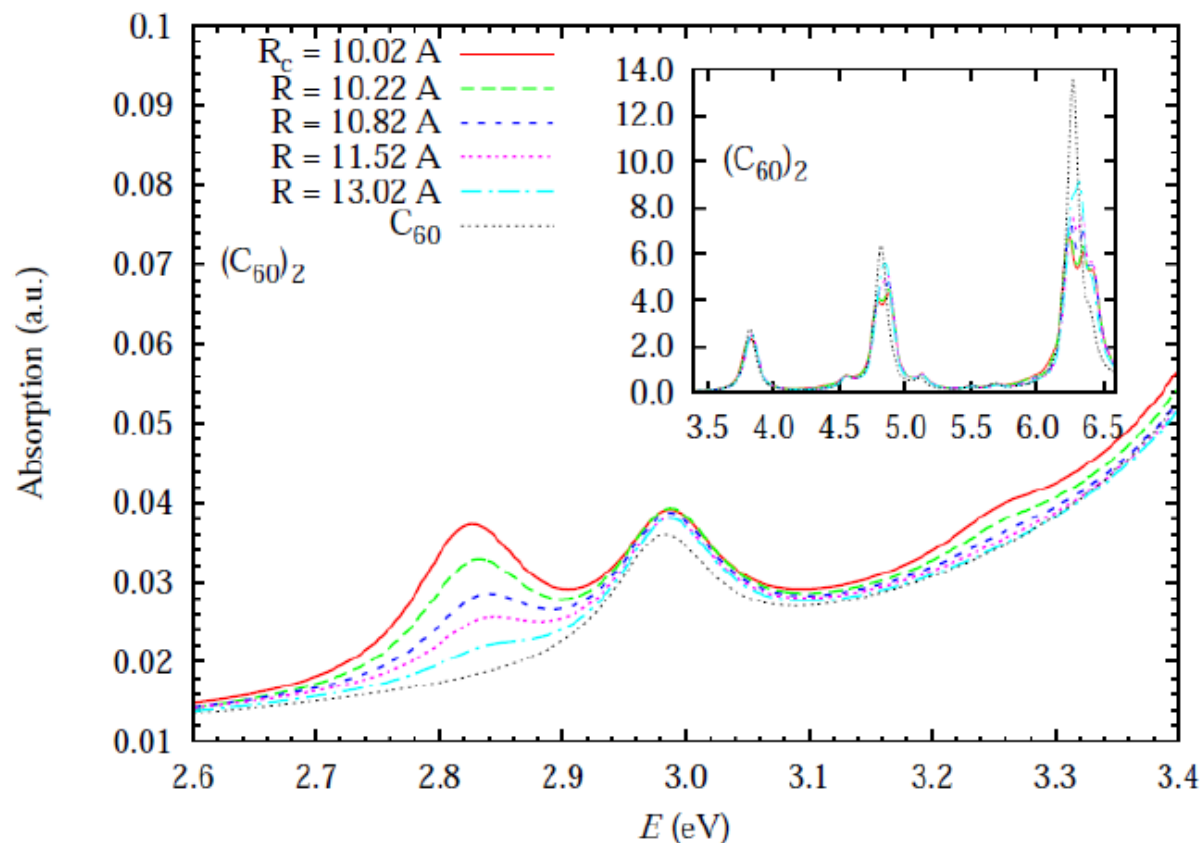


FIG. 3. (Color online) CNDOL theoretical absorption spectra of $(C_{60})_2$ models compared with an isolated C_{60} model. The low energy region (2.6-3.4 eV) of the spectrum is in the main plot, while the zone of the intense bands is shown in the graphic inside. The line width used for band plotting is 0.05 eV. The distance (R) between fullerene centers in $(C_{60})_2$ models increases from the original in the fullerite crystal ($R_c = 10.02 \text{ \AA}$ plotted in red) up to 13.02 \AA .

Modeling C_{60} aggregates

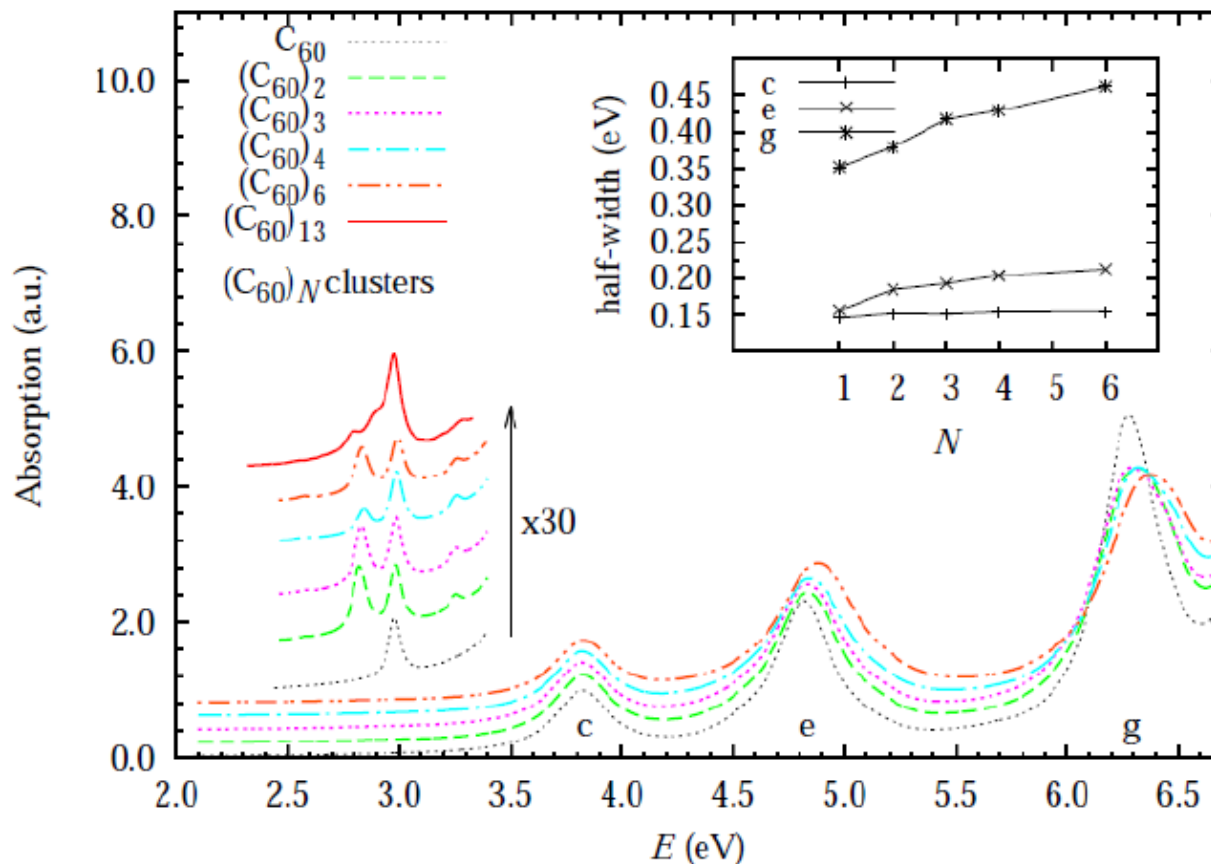


FIG. 4. (Color online) CNDOL theoretical absorption spectra of $(C_{60})_N$ models. The low energy region of the spectrum has been inset amplified $\times 30$. The inside graphic shows half-widths of the c , e and g bands for the $(C_{60})_N$ models where $N = 2, 3, 4$ and 6 . All of $(C_{60})_N$ modeled absorption spectrum intensities has been divided by the N units. Absorption is shown in arbitrary units (a.u.) to allow comparisons.

Modeling C_{60} aggregates

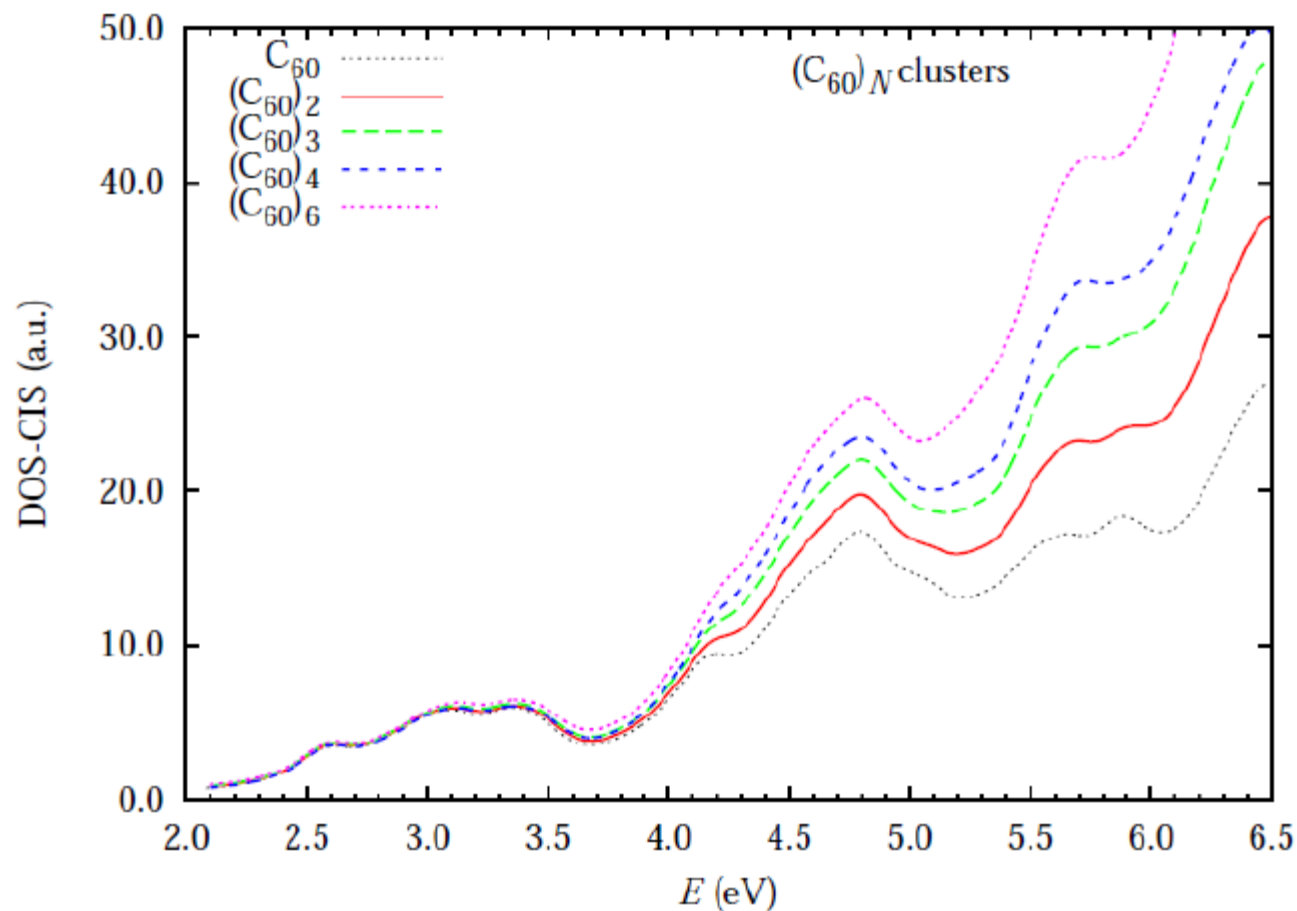


FIG. 5. (Color Online) CNDOL density of CIS states (DOS-CIS) obtained for the study systems. Each DOS is divided by the number of C_{60} units.

ACKNOWLEDGEMENTS

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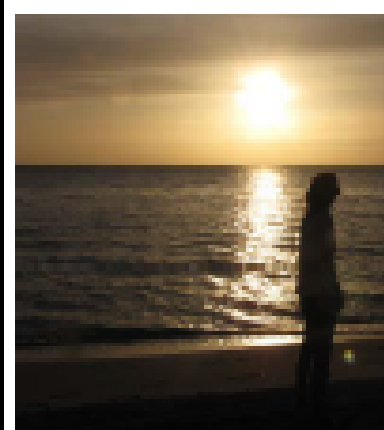
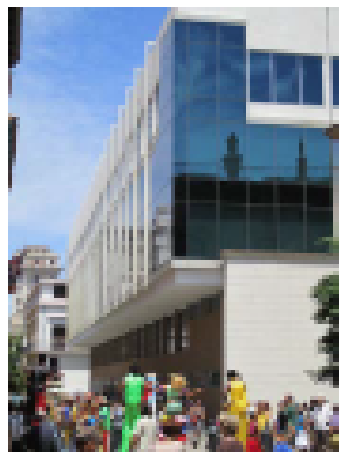
Eduardo Menéndez

Cornell University, Ithaca

Roald Hoffmann



And Wilfredo Lam, for this paints



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