Calculation of optical properties and macroscopic polarization with SIESTA

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Efficient density-functional calculations with atomic orbtitals: a hands-on tutorial on the SIESTA code

CECAM Tutorial

Lyon, June 18-22

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DONOSTIA INTERNATIONAL PHYSICS CENTER
D.I.P.C.

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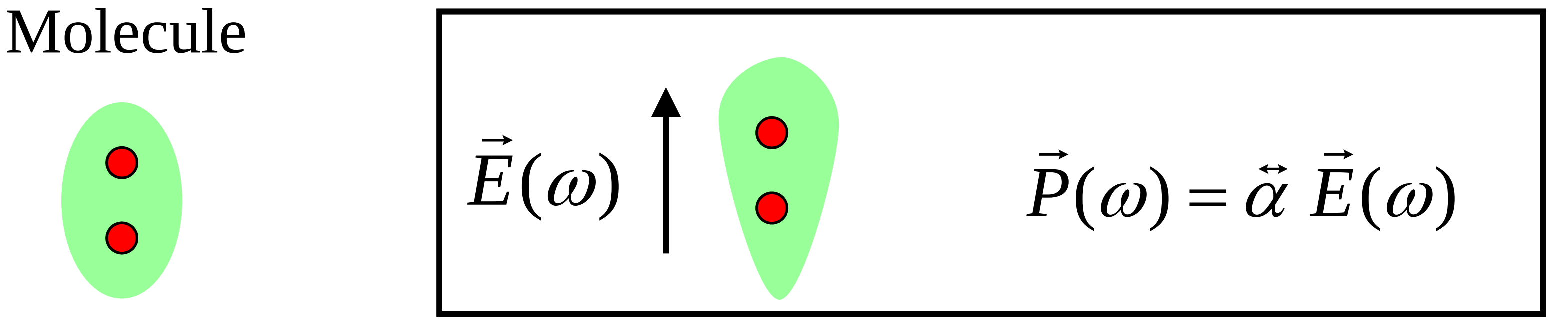
Polarizability



$$\vec{P}(\omega) = \overleftrightarrow{\alpha}\,\vec{E}(\omega)$$

Exact many body wavefunctions and eigenvalues

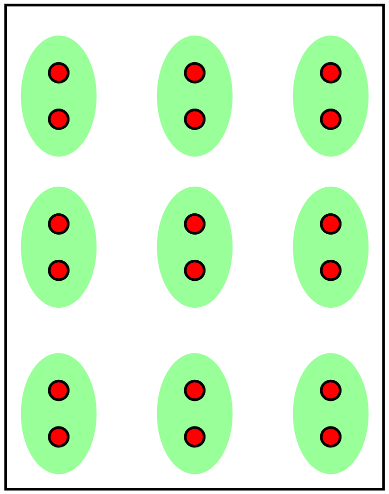
$$\mathrm{Im}[\alpha_{\nu\mu}(\omega)] = \sum_i < \Psi_i \,|\, r_\nu \,|\, \Psi_0 >< \Psi_0 \,|\, r_\mu \,|\, \Psi_i > \delta(E_i - E_0 \pm \omega)$$

Approximation with Kohn-Sham orbitals and eigenvalues

$$\mathrm{Im}[\alpha^0{}_{\nu\mu}(\omega)] = 2\times$$

$$\sum_i \sum_j f_i\,(1 - f_j) < \Phi_i \,|\, r_\nu \,|\, \Phi_j >< \Phi_j \,|\, r_\mu \,|\, \Phi_i > \delta(\varepsilon_i - \varepsilon_j \pm \omega)$$

Dielectric function in solids



$$\mathrm{Im}[\varepsilon_{\nu\mu}(\omega)] \approx \frac{4\pi^2}{V_{mol}} \mathrm{Im}[\alpha_{\nu\mu}(\omega)]$$

Without local field corrections

Unfortunately there is no way to apply this formula to a solid

Position operator is ill-defined for extended wavefunctions

$$< e^{i\vec{k}.\vec{r}} \,|\, \vec{r} \,|\, e^{i\vec{k}.\vec{r}} >= ?$$

Momentum formulation

$$\hat{H} = -\tfrac{1}{2}\nabla^2 + V(\vec{r}) \quad \Rightarrow \quad \boxed{[\hat{r},\hat{H}] = -i\hat{p} = \vec{\nabla}}$$

$$<\Phi_i|[\hat{r},\hat{H}]|\Phi_j> = <\Phi_i|\vec{\nabla}|\Phi_j>$$

$$<\Phi_i|[\hat{r},\hat{H}]|\Phi_j> = <\Phi_i|\vec{r}|\Phi_j>(\varepsilon_j-\varepsilon_i) = <\Phi_i|\vec{\nabla}|\Phi_j>$$

$$\boxed{\begin{aligned}&\mathrm{Im}[\varepsilon^0(\vec{n},\omega)] = 2\times \frac{4\pi^2}{V_{cell}}\\ &\int dk^3 \sum_i \sum_j f_i(1-f_j)\frac{|<\Phi_i(\vec{k})|\vec{\nabla}.\vec{n}|\Phi_j(\vec{k})>|^2}{(\varepsilon_j-\varepsilon_i)^2}\delta(\varepsilon_i-\varepsilon_j\pm\omega)\end{aligned}}$$

A word of caution for non-local potentials

$$\hat{H} = -{}^{1}\!/_{2}\nabla^{2} + V(\vec{r}) + |\chi><\chi|$$

$$\Downarrow$$

$$\boxed{[\hat{r},\hat{H}] = \vec{\nabla} + [\hat{r},V_{NL}]}$$

$$\boxed{\begin{aligned}&<\Phi_i|\vec{r}|\Phi_j>(\varepsilon_j-\varepsilon_i) = <\Phi_i|\vec{\nabla}|\Phi_j> +\\ &<\Phi_i|\vec{r}|\chi><\chi|\Phi_j> - <\Phi_i|\chi><\chi|\vec{r}|\Phi_j>\end{aligned}}$$

No problem: localized objects

Thomas-Reiche-Kuhn or f-sum rule

$$\int d\omega \, \omega \, \mathrm{Im}[\varepsilon(\omega)] = 2\pi^2 N_{val}$$

Drude term for metals (ω→0)

$$\varepsilon_{\nu\mu}(\omega \rightarrow 0) = 1 - \frac{4\pi i}{\omega} \sigma_{\nu\mu}^{Drude}(\omega)$$

$$\sigma_{\nu\mu}^{Drude}(\omega) = \frac{\sigma_{\nu\mu}^{dc}}{1 - i\omega\tau_{eff}}$$

$$\sigma_{\nu\mu}^{dc} = 2 \times \tau_{eff} \sum_{i} \int dk^3 \, v^i{}_{\nu}(\vec{k}) v^i{}_{\mu}(\vec{k}) \, \delta(\varepsilon_i(\vec{k}) - \varepsilon_F)$$

$$v^i{}_{\nu}(\vec{k}) = < \Phi_i(\vec{k}) \,|\, \dot{x}_{\nu} \,|\, \Phi_i(\vec{k}) >$$

Parameters and input

OpticalCalculation : default .false., set to **.true.**

Optical.NumberOfBands : all of them used if not specified

%block Optical.Mesh
$n_1 \quad n_2 \quad n_3$
%endblock Optical.Mesh

Optical.Broaden: small “artificial” broadening, 0.X eV

Optical.PolarizationType: *polarized, unpolarized, polycrystal*

%block Optical.Vector
$E_x \quad E_y \quad E_z$
%endblock Optical.Vector

Either ***E***, electric field
or ***k***, propagation vector

Optical.Vector

Polarized: $\vec{E}$

Unpolarized: $\vec{k} \quad \longleftrightarrow \quad \vec{k} \perp \vec{E}$

Polycrystal: Average over three spatial directions

What is left out in this approach

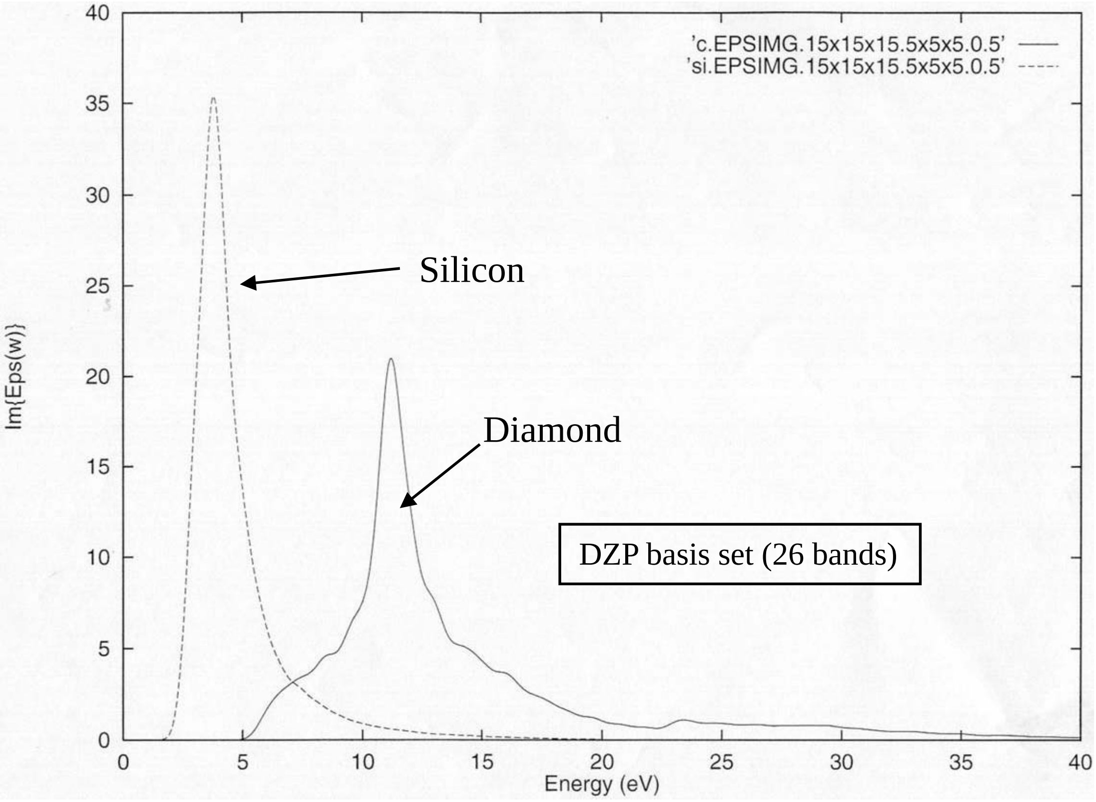
*Classical collective modes (plasmons). They can be included at the RPA level. Important at low energies for small systems, not that much for bulk.

*Excitonic effects (electron-hole interaccion). Quite hard to include

*Spectrum beyon Kohn-Sham approx.
At the moment just the “scissor operator” to correct excitation energies.

Diamond and Silicon

SIESTA

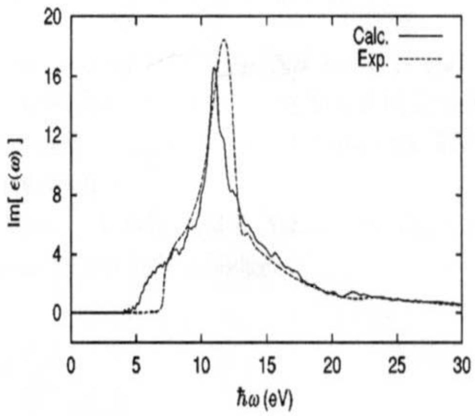


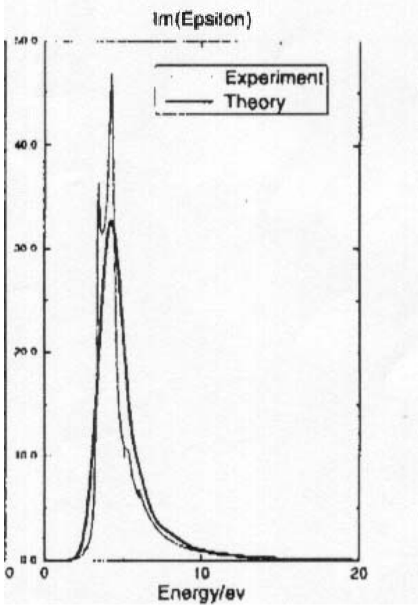
Silicon

Diamond

DZP basis set (26 bands)

G.F. Bertsch *et al*.Phys.Rev. B 62, 7998 (2000).





PW, CASTEP

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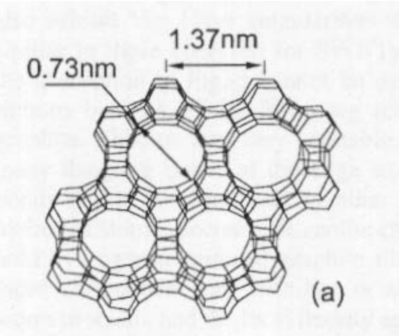
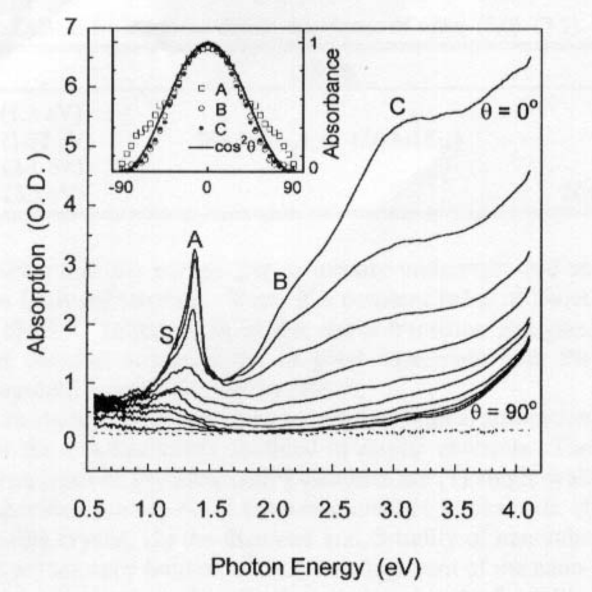
Polarized Absorption Spectra of Single-Walled 4 Å Carbon Nanotubes Aligned in Channels of an $AlPO_4$-5 Single Crystal

Z. M. Li,[1] Z. K. Tang,[1,*] H. J. Liu,[1] N. Wang,[1] C. T. Chan,[1] R. Saito,[2] S. Okada,[3] G. D. Li,[4] J. S. Chen,[4]
N. Nagasawa,[5] and S. Tsuda[5]





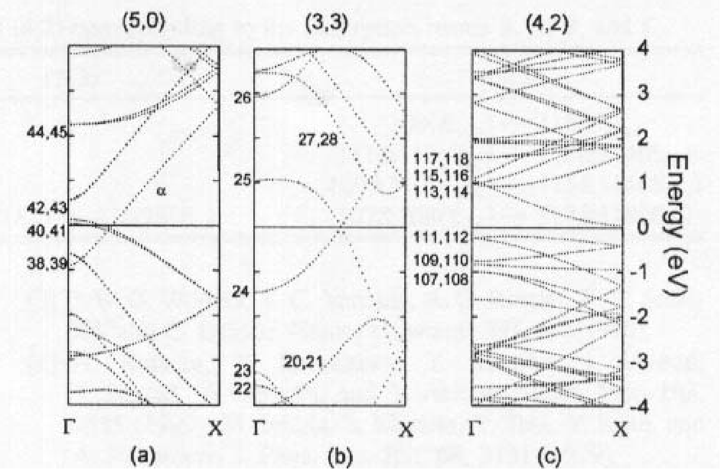


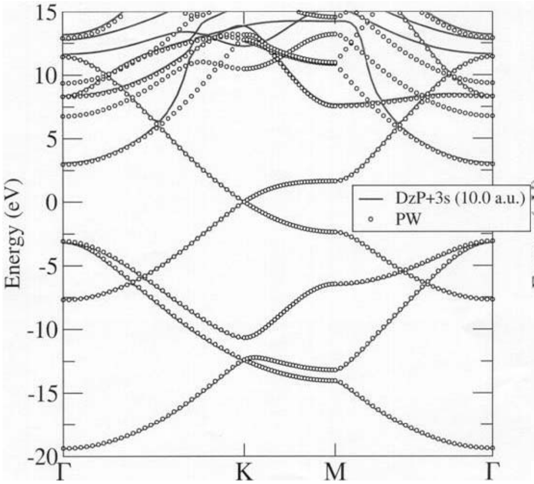
TABLE I. Allowed dipole transitions of tubes (5,0), (3,3), and (4,2) corresponding to the absorption bands S, A, B, and C.

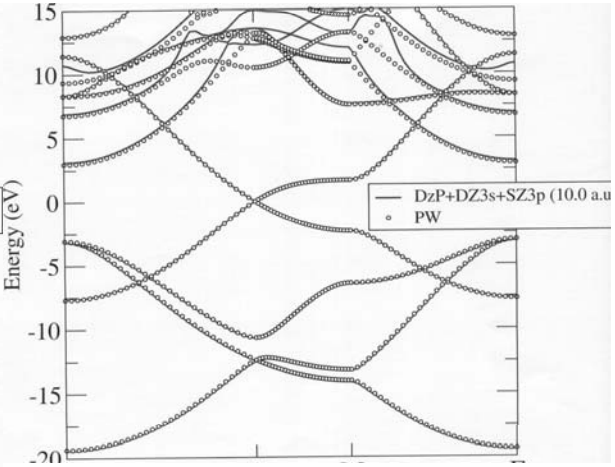
	(5, 0)	(3, 3)	(4, 2)
S (1.2 eV)			$109(E_{10g}) \rightarrow 115(E_{10u})$
A (1.37 eV)	$38\&39(E_{1g}) \rightarrow 42\&43(E_{1u})$		$111\&112(E_{9g}) \rightarrow 113\&114(E_{9u})$
B (2.1 eV)			$109\&110(E_{10g}) \rightarrow 115\&116(E_{10u})$
C (3.1 eV)		$20\&21(E_g) \rightarrow 27\&28(E_u)$	$107\&108(E_{3g}) \rightarrow 117\&118(E_{3u})$

Optical response of 4-Å diameter SWCNT with SIESTA

Testing the accuaracy of SIESTA band structures on graphene:

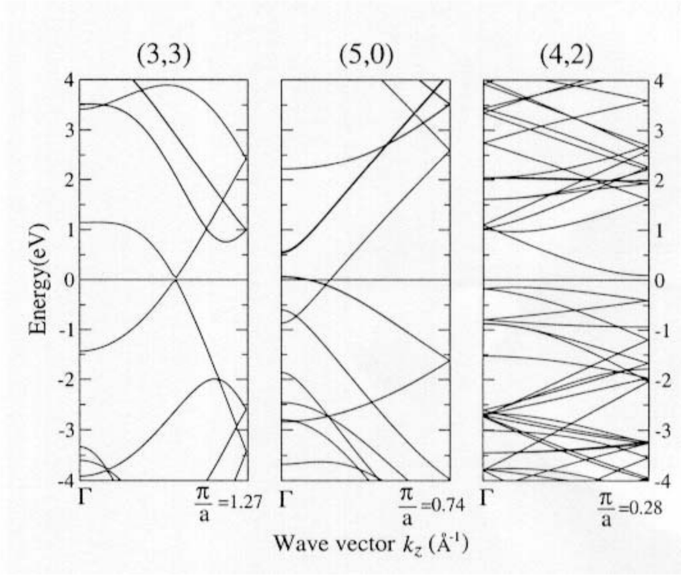
- Including a diffuse 3s orbital we have perfect with PW up to 6 eV
- Adding an additional 3p shell the agreement is extended to 10-12 eV





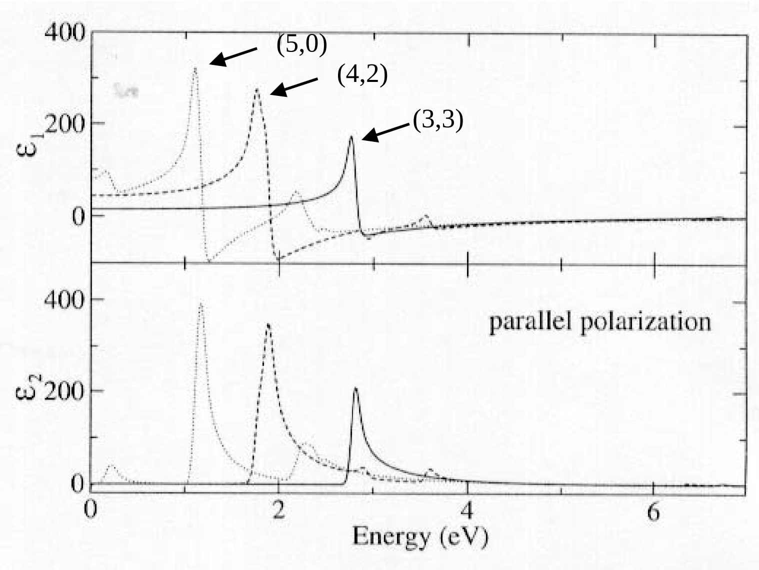
In fact, ...

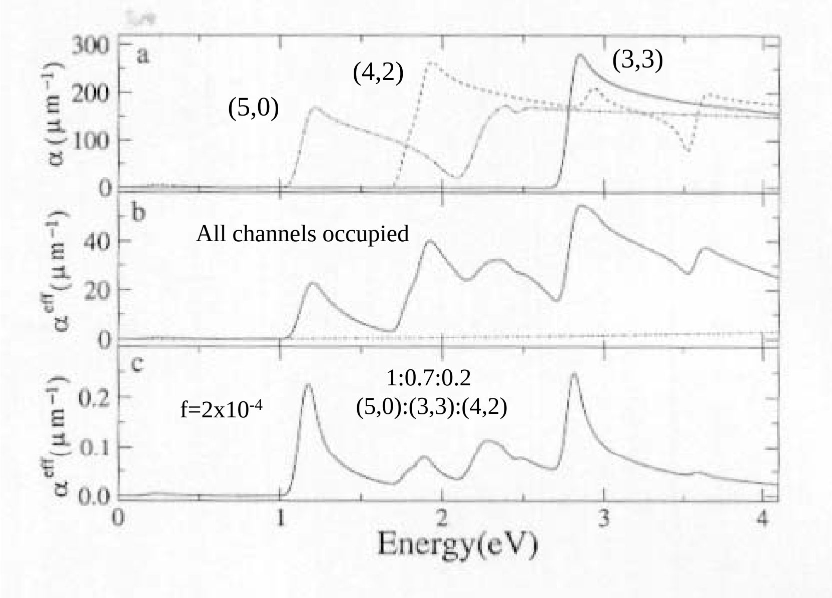
Our band structures for the 4-Å are in very nice agreement with the PW calculations of Li *et al.*

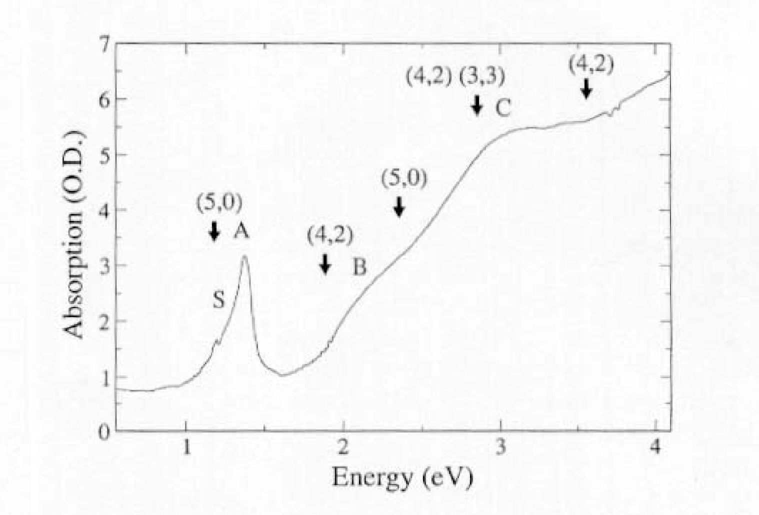


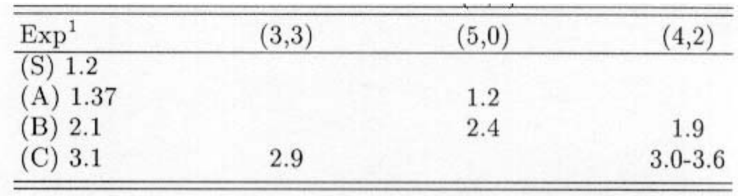
Optical response of 4-Å diameter SWCNT with SIESTA (cont.)

$$\epsilon_{\rm eff}(\omega) = \frac{f[\epsilon_{(3,3)} + \epsilon_{(5,0)} + \epsilon_{(4,2)}]}{3} + (1-f)\epsilon_{\rm zeol}$$









Exp[1]	(3,3)	(5,0)	(4,2)
(S) 1.2			
(A) 1.37		1.2	
(B) 2.1		2.4	1.9
(C) 3.1	2.9		3.0-3.6

TABLE II: Energies in eV of the experimental and calculated optical absorption maxima of the SWNT containing zeolite. The calculated values are aligned to the corresponding experimental peaks.