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Calculation of the Optical Spectra of Atomic Clusters

Computer Simulation using a code based on **SIESTA**

Spanish

Initiative for

Electronic

Simulations of

Thousands of

Atoms



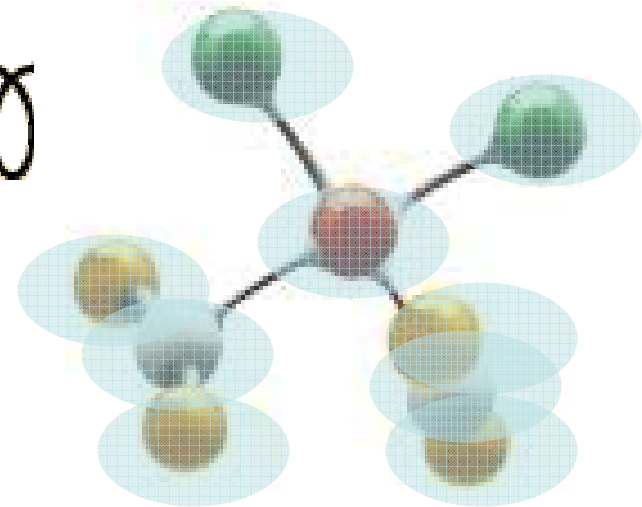
Basic Physical Idea

Get electric properties by looking at how a molecule responds to an Electric field

- Molecule subjected to constant electric field

- Electric field is switched off 

⇒ The dipole moment of the molecule begins to oscillate



- Electric Polarizability: $\alpha(\omega) = \text{Dipole}(\omega) / E(\omega)$

Quantum Mechanics

- How do we know how the electrons respond in time?

$$i\hbar \frac{\partial}{\partial t} \Psi = \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(r,t) + e^2 \int \frac{\rho(r',t)}{|r-r'|} dr + V_{xc}[\rho](r,t) \right] \Psi$$

- Write ψ in terms of Gaussian wave functions φ :

$$\Psi = c_1 \varphi_1 + c_2 \varphi_2 + c_3 \varphi_3 + \dots$$

- In terms of the coefficients c the Schroedinger equation becomes:

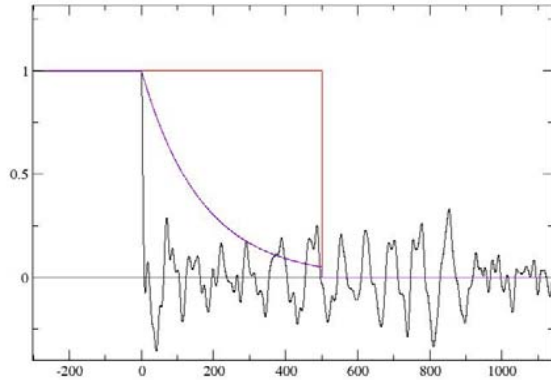
$$i\hbar \frac{\partial}{\partial t} c = S^{-1} H c$$

where S is the overlap matrix between the Gaussian wave functions (we need it because the Gaussians are not all orthogonal)

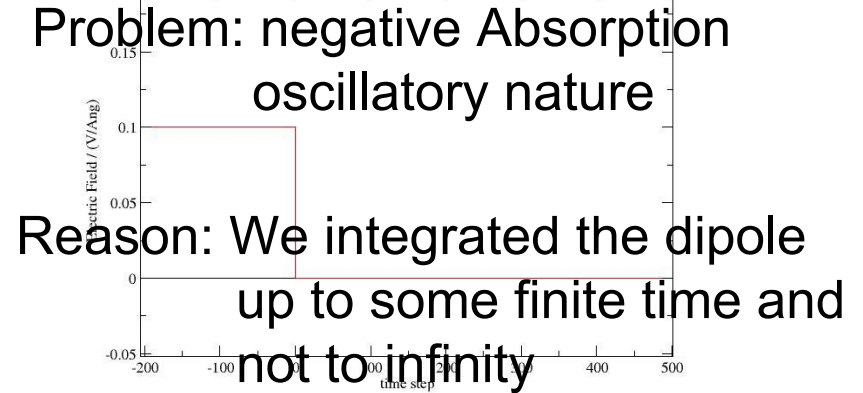
Dipole and Electric Field versus time for

C

Dipole vs time



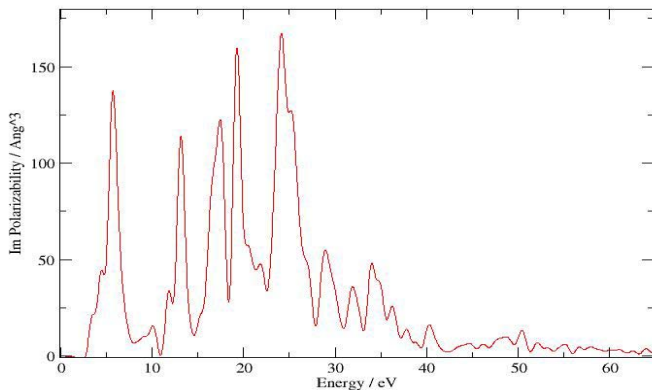
Electric Field vs Time
time step=2Ryd



Electric Polarizability:

$$\alpha(\omega) = \text{Dip}(\omega) / E(\omega)$$

Im Polarizability vs Energy for C60



Solution: Damping- multiply the
Dipole(t) by a decaying
exponential...
...or a polynomial

(...by the way, I've written the
code that calculates $\alpha(\omega)$)

Self-consistency Tests for C60

Sum-rule: $N_e = \int_0^{\infty} S(\omega) d\omega$ where $S(\omega) = \frac{2m}{\pi e^2 \hbar} \omega \text{Im} \alpha(\omega)$

Theoretical value: $N_e = 60 \cdot 4 = 240$

Calculated: $N_e = 245$

Static Polarizability: $\alpha(0) = \frac{2}{\pi} \int_0^{\infty} \frac{\text{Im} \alpha(\omega)}{\omega} d\omega$

LHS: $\alpha(0) = \frac{\text{Dip}(0)}{E(0)} = 76.1 A^3$

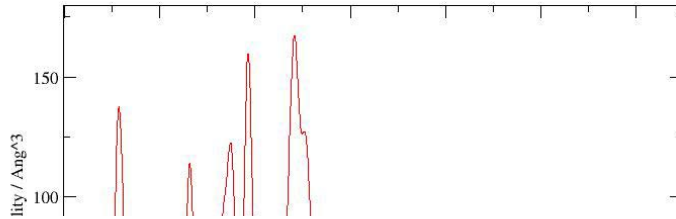
RHS: $\alpha(0) = 76.0 A^3$

Experiment: $\alpha(0) = 79.3 A^3$ ¹

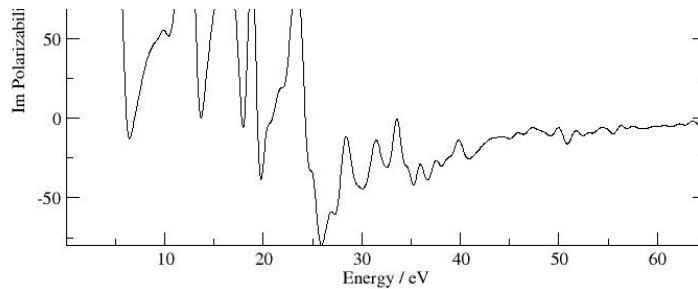
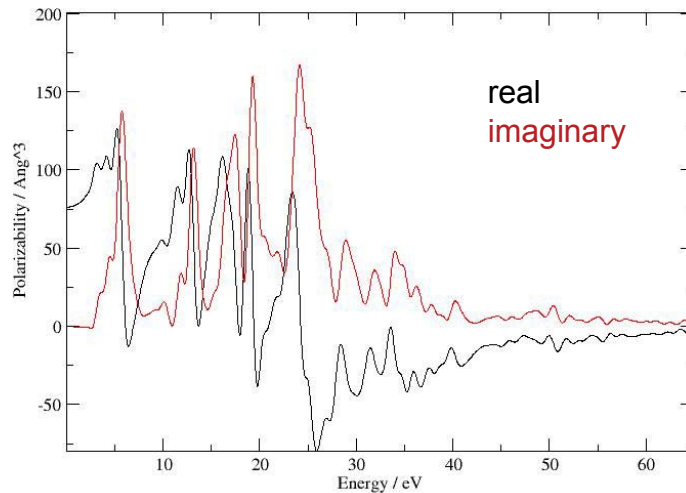
¹ J.S. Meth, H. vanherzeele, and Y. Wang, Chem. Phys. Lett. **197**, 26 (1992)

Test the Kramer's Kronig Relations

Im Polarizability vs Energy for C60



Polarizability vs Energy for C60

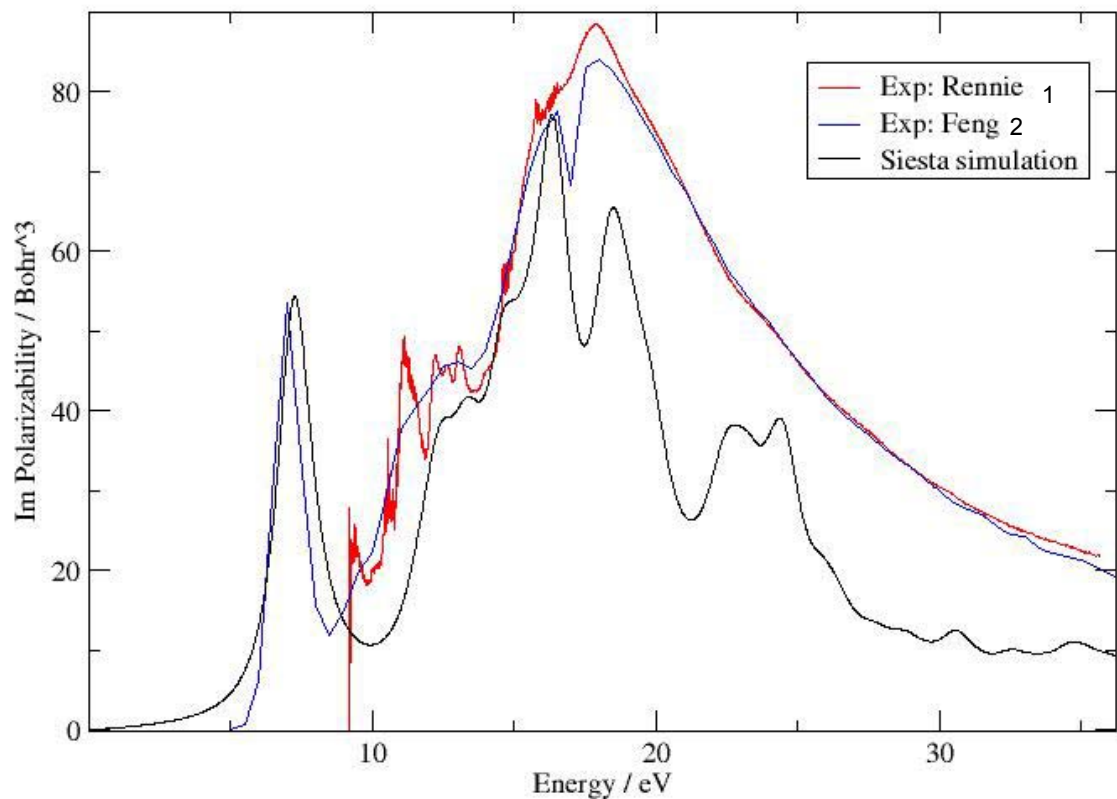


Consequence of the Kramer's Kronig relations:

The real part of the polarizability decreases as a function of energy where there is an absorption pole

Comparison with Experiment for Benzene

Im Polarizability vs Energy for Benzene



Good enough for government work!!!

¹ E.E. Rennie, C.A.F. Johnson, J.E. Parker, D.M.P. Holland, D.A. Shaw, and M.A. Hayes, "A photoabsorption, photodissociation and photoelectron spectroscopy study of C₆H₆ and C₆D₆," Chem. Phys. **229**, 107-123 (1998).

² R. Feng, G. Cooper, and C.E. Brion, "Dipole (e,e) spectroscopic studies of benzene: quantitative photoabsorption in the UV, VUV and soft x-ray regions," J. Electron Spectrosc. Related Phenom. **123**, 199-209 (2002).

Improve Efficiency of Code - more Quantum

- Remember: $i\hbar \frac{\partial}{\partial t} \Psi = H\Psi$ In gaussian basis: $i\hbar \frac{\partial}{\partial t} c = S^{-1}Hc$

$$c(t + \Delta t) = e^{-\frac{i}{\hbar} \int_t^{t+\Delta t} S^{-1} H(t') dt'} c(t) \quad \Rightarrow \quad c(t + \Delta t) \approx e^{-\frac{i}{\hbar} S^{-1} H \Delta t} c(t)$$

H is a matrix, evaluating the exponential would require diagonalization
 \Rightarrow do Taylor expansion (or something similar) instead

- Two ways of approximating the exponential:

$$1. \text{ Crank-Nicholson } c(t + \Delta t) \approx \frac{1 - \frac{i}{\hbar} S^{-1} H \Delta t / 2}{1 + \frac{i}{\hbar} S^{-1} H \Delta t / 2} c(t)$$

Which one is better?

$$2. \text{ Leapfrog } c(t + \Delta t) \approx c(t - \Delta t) - 2 \frac{i}{\hbar} S^{-1} H \Delta t c(t)$$

Is there another algorithm that's faster?

Comparing Leapfrog and Crank-Nicholson Iteration procedures for C_{60}

- Computation times:

Expectation: Leapfrog is much faster because it doesn't involve matrix inversion

A closer look: Matrix inversion turns out to be not much slower than multiplication (2.7s vs 2.6s) and is small compared to the total computational time inside a cycle.

Code	Computation time for a complete iteration
Crank-Nicholson	26.9s
Leapfrog	23.2s

- The max time step size Δt :

Crank-Nicholson: $\Delta t = .2 / \text{Ryd}$

Leapfrog: $\Delta t = .035 / \text{Ryd}$

=> The Crank-Nicholson method is about 5 times faster!

Conclusions

- Siesta simulation results are in reasonable agreement with experimental results
- The Crank-Nicholson time evolution is more efficient (by a factor of about 5) than the Leapfrog method
- No success of improving on Leapfrog