

Real time calculation of optical spectra of atomic clusters using time dependent local density approximation (LDA)

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August 2005

We present an approach for obtaining optical spectra using a real time calculation which employs a code that is based on Siesta. Simulation results for benzene and C₆₀ are compared with experiment. Further, two versions of the code, which use different methods of time evolution of the wave function, are compared in efficiency.

Theory

The optical properties of a molecule are obtained from its response to a perturbing electric field. In our case, the electric field is chosen to be a step function

$$E(t) = E_0(1 - \theta(t)) \quad (1.)$$

where $\theta(t)$ is the unit step function. The perturbing field displaces the electrons of the molecule, which gives rise to a time varying electric dipole by means of which optical properties can be obtained.

For $t < 0$, the molecule is put in a constant electric field and the system is solved for the ground state. At $t = 0$, the perturbing field is switched off and Schrödinger's equation

$$i\hbar \frac{\partial}{\partial t} \Psi = H\Psi \quad (2.)$$

is used to propagate the one-electron wave functions Ψ . (Atomic units $\hbar = m = e = 1$ will be used for the remainder of this report.) The Hamiltonian in (2) is given by¹

$$H = \frac{1}{2} \nabla^2 + V_{\text{ext}}(r, t) + \int \frac{\rho(r', t)}{|r - r'|} dr' + V_{\text{xc}}[\rho](r, t) \quad (3.)$$

Because core electron transitions occur only at essentially frozen optical frequencies, only the valence electron wave functions are propagated. The effect of the core electrons is incorporated as pseudopotentials in the

external potential V_{ext} . Apart from the contributions due to core electrons, the external potential V_{ext} is also composed of the energy due to the applied electric field and the potential due to the nuclei. It is of importance to note that the variation in internuclear distances, which occurs due to thermal fluctuations, has been ignored. This variation, which is usually incorporated using Debye-Waller factors, causes broadening of the optical spectrum.

The last term on the right of (3.) is the exchange correlation potential V_{xc} that arises from the fact that Ψ is a single-electron rather than a full-electron, wave function. Physically, the effect of V_{xc} can be interpreted as an electron-electron repulsion due to the Pauli exclusion principle. The calculation of V_{xc} is done using the local density approximation, which assumes that V_{xc} is a function of the local density at time t only.

Time evolution of Ψ is done in a basis consisting of Gaussian functions that are used to model atomic orbitals. In this basis, the Ψ is propagated according to the unitary time evolution operator

$$c(t + \Delta t) = e^{-i \int_t^{t+\Delta t} H(t') dt'} c(t) \approx e^{-i S^{-1} H \Delta t} c(t) \quad (4.)$$

where the overlap matrix S arises from the fact that the Gaussian orbitals are in general not orthogonal.¹

An exact evaluation of the right hand side of equation (4.) would require diagonalization of the exponent. For C_{60} , one of the molecules studied, each carbon atom has 13 Gaussian orbitals in the primitive basis, adding up to a total of 780 basis orbitals. Because the diagonalization of a 780x780 matrix is time inefficient, the exponential in (4.) is approximated with the Crank-Nicholson operator¹

$$c(t + \Delta t) \approx \frac{1 - iS^{-1}H\Delta t/2}{1 + iS^{-1}H\Delta t/2} c(t) + O(\Delta t^2). \quad (5.)$$

This formalism has the advantage that the unitary property of the time evolution operator is retained, which guaranties that the wave functions remain normalized.

At every time step, the electric dipole $D(t)$ is calculated from the wave functions $c(t)$. The linear polarizability $\alpha(\omega)$ can be computed from the ratio of the electric dipole and electric fields in frequency space, i.e.

$$\alpha(\omega) = D(\omega) / E(\omega) \quad (6.)$$

where $D(\omega)$ and $E(\omega)$ are the Fourier transforms of $D(t)$ and $E(t)$, respectively. It should be noted that the polarizability is in general a 3x3 matrix. However, since molecules in fluids and gases molecules are oriented in random directions, only rotationally invariant quantities are physically interesting. We therefore construct the (rotationally invariant) average linear polarizability

$$\langle \alpha(\omega) \rangle = \frac{1}{3} Tr \{ \alpha_{ij}(\omega) \} \quad (7.)$$

In order to compute the trace of $\alpha(\omega)$, three simulations with electric fields along different axes have to be carried out.

Using the field in (1.), we obtain from the expression for $\alpha(\omega)$ in (6)¹

$$\alpha(\omega) = D_0 / E_0 + i\omega D_{t>0}(\omega) / E_0 \quad \text{for } \omega > 0 \quad (8.)$$

where D_0 is the at time zero. $D_{t>0}(\omega)$ is the Fourier transform of the dipole moment for times $[0, T]$, where T is the total simulated time. In order to avoid end ripples in $D_{t>0}(\omega)$, $D(t)$ is multiplied by a polynomial windowing function before taking the Fourier transform. Apart from getting rid of the end ripples, the windowing function also has the effect of broadening the frequency spectrum. Physically, this may be regarded a means of incorporating the broadening arising from Debye-Waller factors. Additional broadening may be incorporated by an exponential damping factor δ . The Fourier transform of $D(t)$ then becomes

$$D_{t>0}(\omega) = \int_0^T e^{i\omega t - \delta t} \left(1 - 3\frac{t^2}{T^2} + 2\frac{t^3}{T^3} \right) D(t) d\omega \quad (9.)$$

Apart from the electric dipole, quadrupole and higher order moments, which arise from the spatial dependence of the electric field, also contribute to the polarizability. However, these corrections are negligible. This can be seen from Fermi's golden rule, by which the absorption is given by

$$\mu \propto \left| \langle \Psi_{initial} | p \cdot A | \Psi_{final} \rangle \right|^2 \quad (10.)$$

where $A = A_0 e^{i\vec{k} \cdot \vec{r}}$ is the vector potential, and $\Psi_{initial}$ and Ψ_{final} are the molecular wave functions of the valence electrons before and after a photon is absorbed. Since r is of the order of the size of an atom, $\vec{k} \cdot \vec{r} \ll 1$ in the optical spectrum.

Therefore, the exponential $e^{i\vec{k} \cdot \vec{r}}$ may be approximated to be unity. In this limit, the operator $p \cdot A$ in (9) becomes a simple dipole operator. Thus in the limit where spatial variations in the perturbing field are negligible, only the dipole term needs to be considered.

Besides the linear polarizability $\alpha(\omega)$, the dipole strength function $S(\omega)$ is also of particular interest. The two quantities are related by

$$\alpha(\omega) = P \int_0^{\infty} \frac{S(\omega') d\omega'}{\omega'^2 - \omega^2} \quad (11.)$$

Performing a contour integration over the upper half plain, we obtain

$$S(\omega) = \frac{2}{\pi} \text{Im} \alpha(\omega). \quad (12.)$$

The importance of the oscillator strength is that it is proportional to the absorption crosssection, which is measured by most experiments. Further, $S(\omega)$ provides an internal consistency test. The integral of $S(\omega)$ over all frequencies should yield the number of electrons N_e present in the molecule, that is

$$N_e = \int_0^{\infty} S(\omega) d\omega \quad (13.)$$

In addition, the integral of $\alpha(\omega)$ provides another test for consistency. Performing a contour integration and assuming that $\alpha(\omega)$ is analytic, it is easily verified that

$$\alpha(0) = \frac{2}{\pi} \int_0^{\infty} \alpha(\omega) d\omega \quad (14.)$$

Hence, the above equation may be regarded as an analyticity test of the polarizability.

Simulation Results

A. Benzene

In order to test the accuracy of our model, we have carried out simulations on benzene. Here, 1000 time steps of size $\Delta t = .2/\text{Hartree}$ were used when the electric field was in the plane of the molecule. However, when the field was oriented perpendicular to the molecule, a smaller time step of $\Delta t = .02/\text{Hartree}$ was needed to achieve

convergence. A possible explanation is that the absorption peaks resulting from a field perpendicular to the molecule were at higher frequency and thus needed a better time resolution.

The primitive basis set used consists of two 1s and one 2p Gaussian orbitals for each hydrogen atom and a total of 13 orbitals for carbon (two s-, six p-, and five d-orbitals). In figure 1, the electric dipole is plotted as a function of time. Figure 2 compares the calculated oscillator strength (black) with experimental results for the absorption crosssection (red² and blue³). The scaling has been chosen so that the magnitude of the absorption peak at $\sim 7\text{eV}$ matches with that of the experiments. Further, an exponential damping factor of $\delta = .02$ Hartree was incorporated in order to achieve the same the width of the 7eV absorption peak as in the experiments.

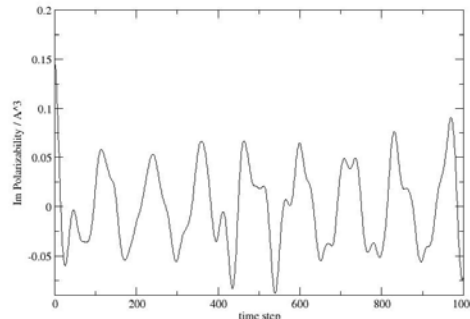


Fig. 1.: Electric Dipole versus time step for benzene

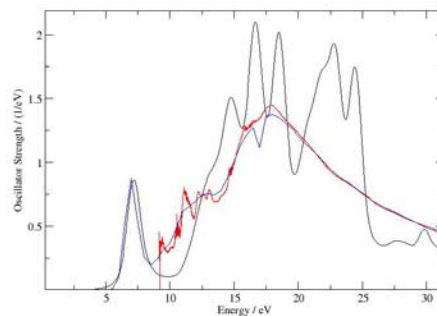


Fig. 2.: Oscillator strength versus energy for benzene: our simulation (black), experiment (red² and blue³)

Comparison with the experimental results gives reasonably good agreement for the low energy spectrum. However, as the energy is increased, the agreement diminishes. A possible reason for the discrepancy between experiment and our calculations can be found in the incompleteness of the basis set used. At higher energies, the electrons tend to occupy states that are not well represented in the basis set used.

The simulation results are further compared with experiment⁴ in figure 3. Figure 4 plots our simulation results (grey), calculations by Walker et al⁵ (black and purple) and further experimental results⁶ (light blue). Again, the calculated results are in approximate agreement with experiments and with other computational results.

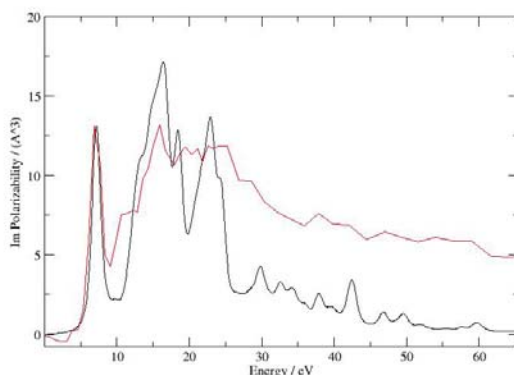


Fig. 3.: Calculated imaginary part of the polarizability (black) and experimental results for absorption (red³) for benzene

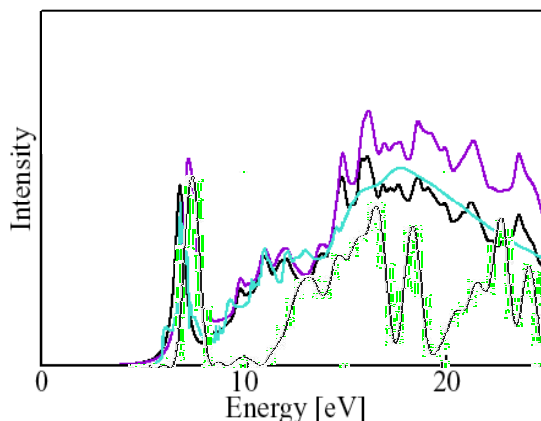


Fig. 4.: Comparison of the absorption spectrum obtained by Walker et al⁴ (black and blue), experiment⁵ (light blue), and our simulation results (light grey) on benzene

The integrated number of valence electrons in Benzene is 29.5, compared to the actual number of 30. Thus the sum rule is satisfied. The integral test for the static polarizability also gives good results. The integrated static polarizability and the polarizability at zero frequency are both equal to 9.26\AA^3 .

B. C₆₀

A similar simulation is done on C₆₀. The basis set used for carbon is the same as that for Benzene. The step size and the total simulated time are 0.1/Hartree and 200/Hartree, respectively. The calculated absorption spectrum is shown in figure 5. As for benzene, the self-consistency tests are highly accurate. The sum rule yields 245.7 out of 240 valence electrons and the left- and right-hand side of equation (14) give 76.1\AA^3 and 76.2\AA^3 , respectively. The results for the static polarizability are further in approximate agreement with the experimental results of 88.2\AA^3 by Meth et al.,⁷ and 79.3\AA^3 from uv absorption⁸.

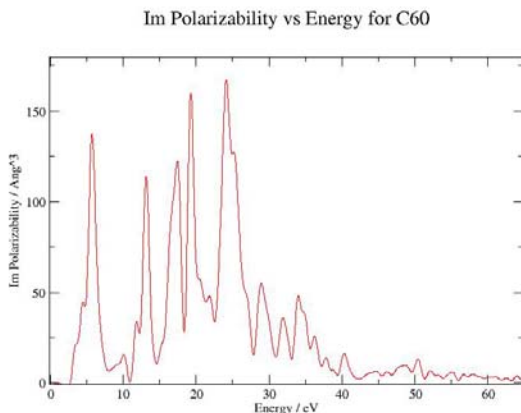


Fig. 5.: Our simulation results for the imaginary part of the polarizability versus energy for C_{60} , $\delta=0$

Comparison of two Methods

In order to increase the efficiency of the code, an alternative approach to approximating the time propagation operator in equation (4) was developed. In particular, the Crank-Nicholson operator in (5) is replaced by a “leapfrog method” of iteration

$$c(t + \Delta t) \approx c(t - \Delta t) - 2iS^{-1}H\Delta t c(t) + O(\Delta t^2). \quad (13)$$

The new method has the advantage that it involves fewer matrix operations and does not involve matrix inversion. After examining computation times for C_{60} , it was found that both codes used an inefficient routine called “matmul” for the matrix multiplication of S^{-1} and H . After “matmul” was replaced by a more efficient routine called “zgemm”, the respective computation times for the Crank-Nicholson and leapfrog codes on single Pentium4 processor were found to be 26.9s and 23.2s. The reason why the leapfrog method is not that much faster is that most of the computation time is not spent evolving the wave function, but is instead used for calculating the Hamiltonian.

Further, the maximal time step for C_{60} was compared for both codes. It was found that for the Crank-Nicholson code, a step size of 0.4/Hartree was sufficient, while the leapfrog method required a step size of 0.08/Hartree (see figures 6 and 7). Hence, the Crank-Nicholson code is overall by a factor of about four faster than leapfrog.

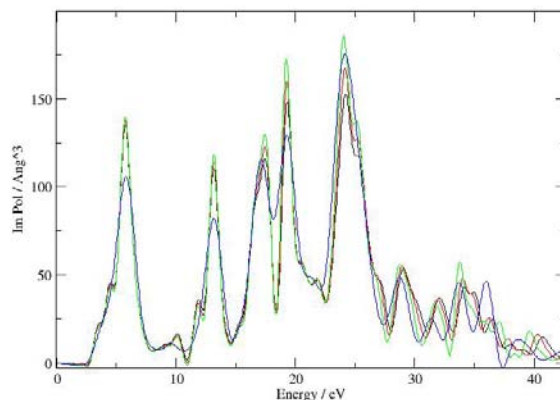


Fig. 6.: Our simulation results for the imaginary part of the polarizability for C_{60} using the “Crank-Nicholson method” for various time steps: 0.2/Hartree (black), 0.4/Hartree (red), 0.6/Hartree (green), 0.8/Hartree (purple)

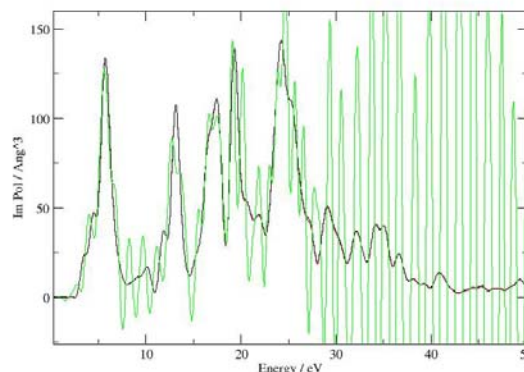


Fig. 7.: Our simulation results for the imaginary part of the polarizability for C_{60} using the “leapfrog method” for various time steps: 0.05/Hartree (black), 0.08/Hartree (red), 0.1/Hartree (green)

Conclusions

For the molecules studied, the Crank-Nicholson time evolution is more efficient than the “leapfrog method”. It

appears that it is the unitary property of the Crank-Nicholson operator allows for a larger choice of the step size. The larger time step more than compensates slightly longer CPU time per iteration of the Crank-Nicholson method.

Further research can be done on the calculation of nonlinear susceptibilities. The main obstacle is to achieve convergence of the codes for strong electric fields.

Moreover, computations times could be greatly reduced if the code were run on parallel. The increased speed of the code would then allow to compute optical spectra of large atomic clusters.

Acknowledgements

I would like to thank Professor John Rehr, the rest of the Rehr group, and Dr. Argyrios Tsolakidis for their advice and guidance.

References

- [1] A. Tsolakidis, D. Sanchez-Portal. And R. M. Martin, "Calculation of the optical response of atomic clusters using time-dependent density functional theory and local orbitals," *PhysRevB*.66.235416
- [2] 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).
- [3] 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).
- [4] Fister, personal discussion
- [5] Walker et al., unpublished manuscript
- [6] E. E. Koch and A. Otto, *Chem. Phys. Lett.* 12, 476 (1972)
- [7] J. S. Meth, H. vanherzeele, and Y. Wang, *Chem. Phys. Lett.* **197**, 26 (1992)
- [8] S. L. Ren, Y. Wang, A. M. Rao, E. McRae, J. M. Holden, T. Hager, K. Wang, Wen-Tse Lee, W. F. Ni, J. Selegue, and P. C. Eklund, *Appl. Phys. Lett.* **59**, 2678 (1991)