RT-TDDFT

Real Time Time-Dependent Density Functional Theory

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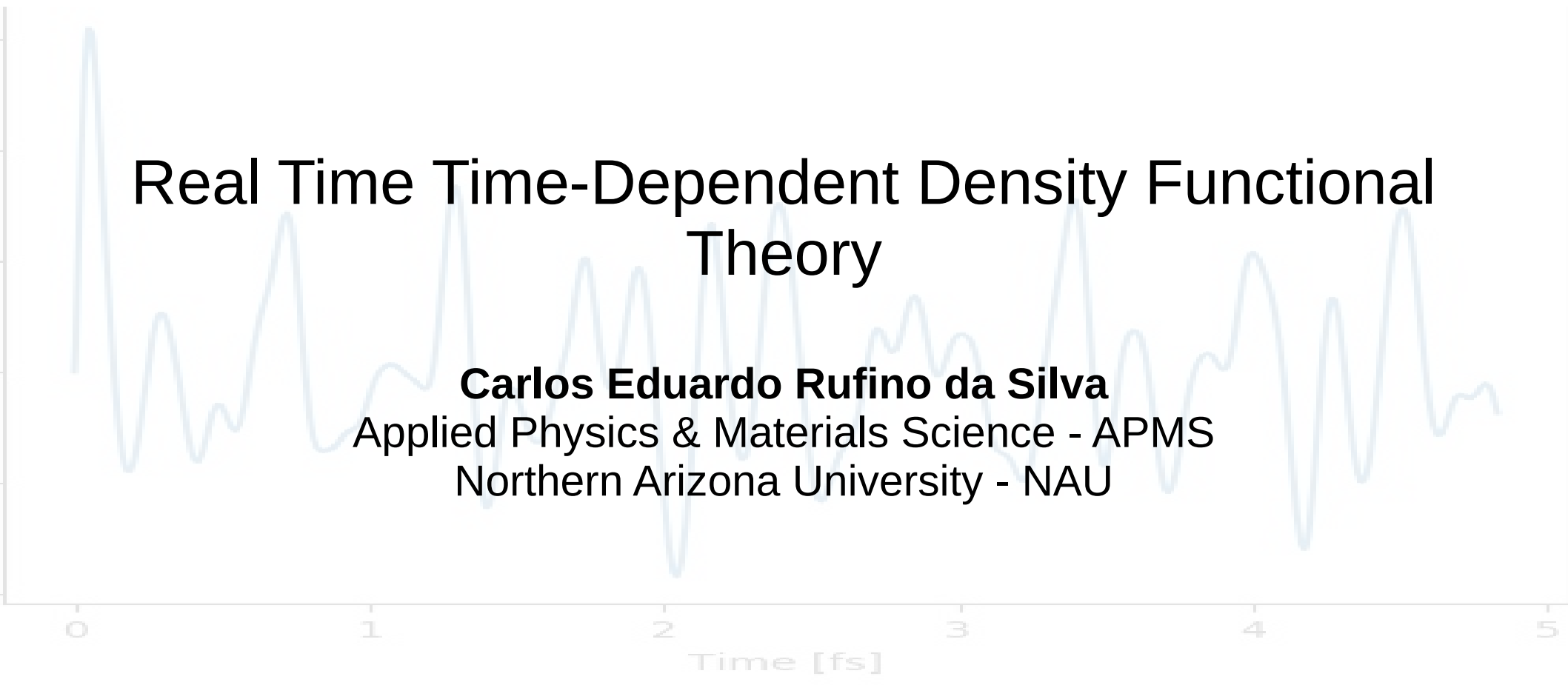


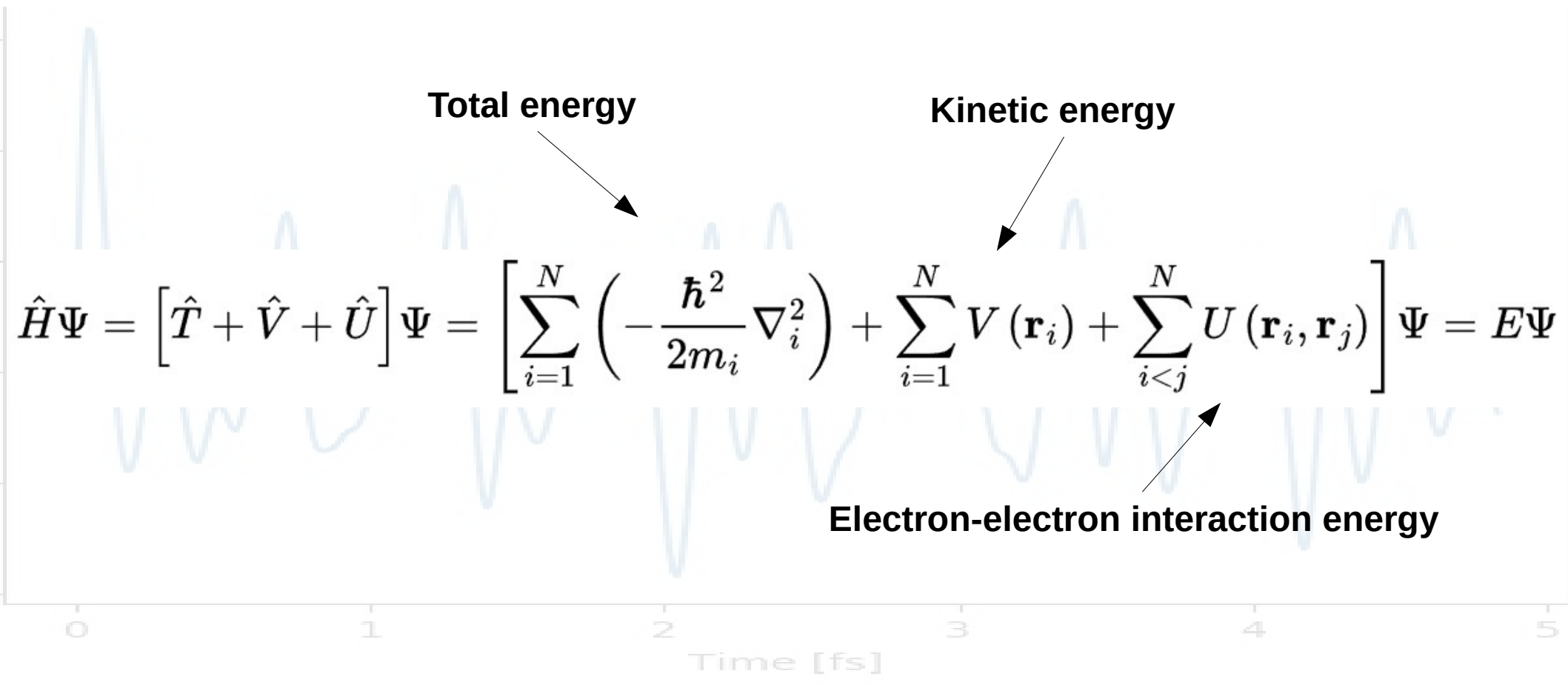
Schrödinger equation

Total energy

Kinetic energy

$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U}\right]\Psi = \left[\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right) + \sum_{i=1}^{N} V(\mathbf{r}_i) + \sum_{i<j}^{N} U(\mathbf{r}_i, \mathbf{r}_j)\right]\Psi = E\Psi$$

Electron-electron interaction energy



First of all, what is DFT?

- Density Functional Theory.
- Computational Quantum Mechanical modeling method.

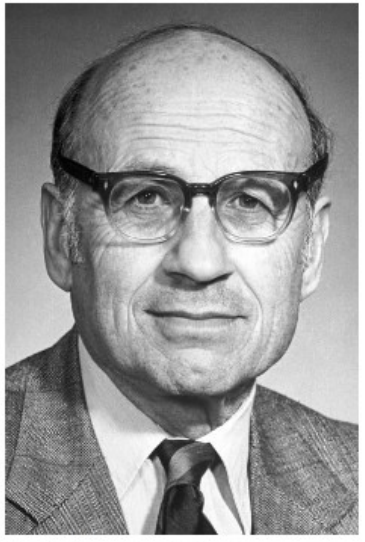
➔ **What is a functional?**

✗ Functions of another function.

➔ **Density?**

✗ The spatially dependent electron density.

The Nobel Prize In Chemistry 1998



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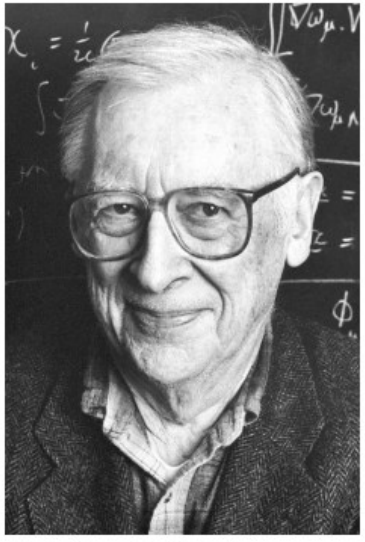
Walter Kohn

Prize share: 1/2



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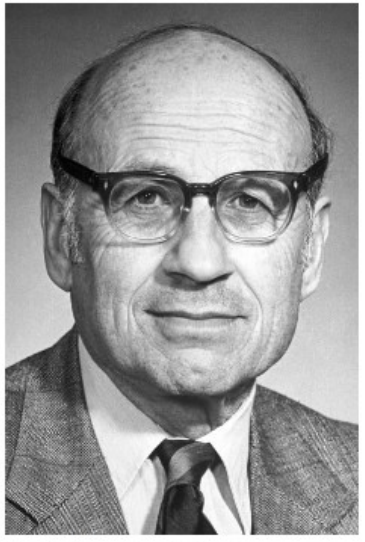
DFT can be be used to:

- Investigate electronic structure of many-body systems (atoms, molecules, condensed phase).
- Investigate magnetic and structural properties of many-body systems.
- Help understand how materials and devices behave and operate under different conditions.

The Nobel Prize In Chemistry 1998



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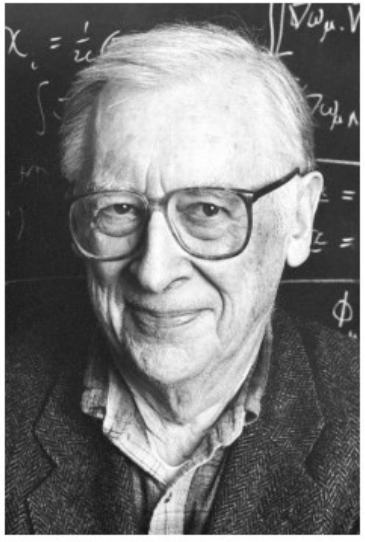

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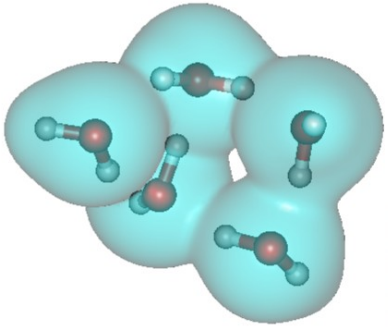
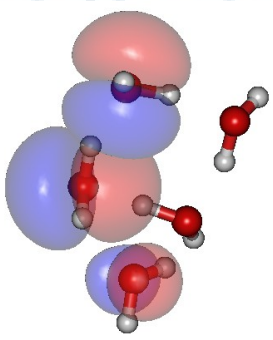
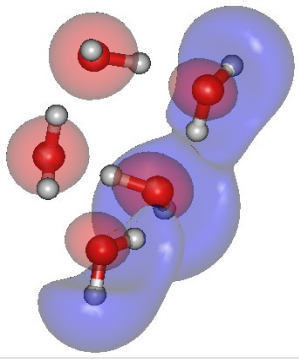
DFT example: Water gas-phase cluster – Vibrational spectra



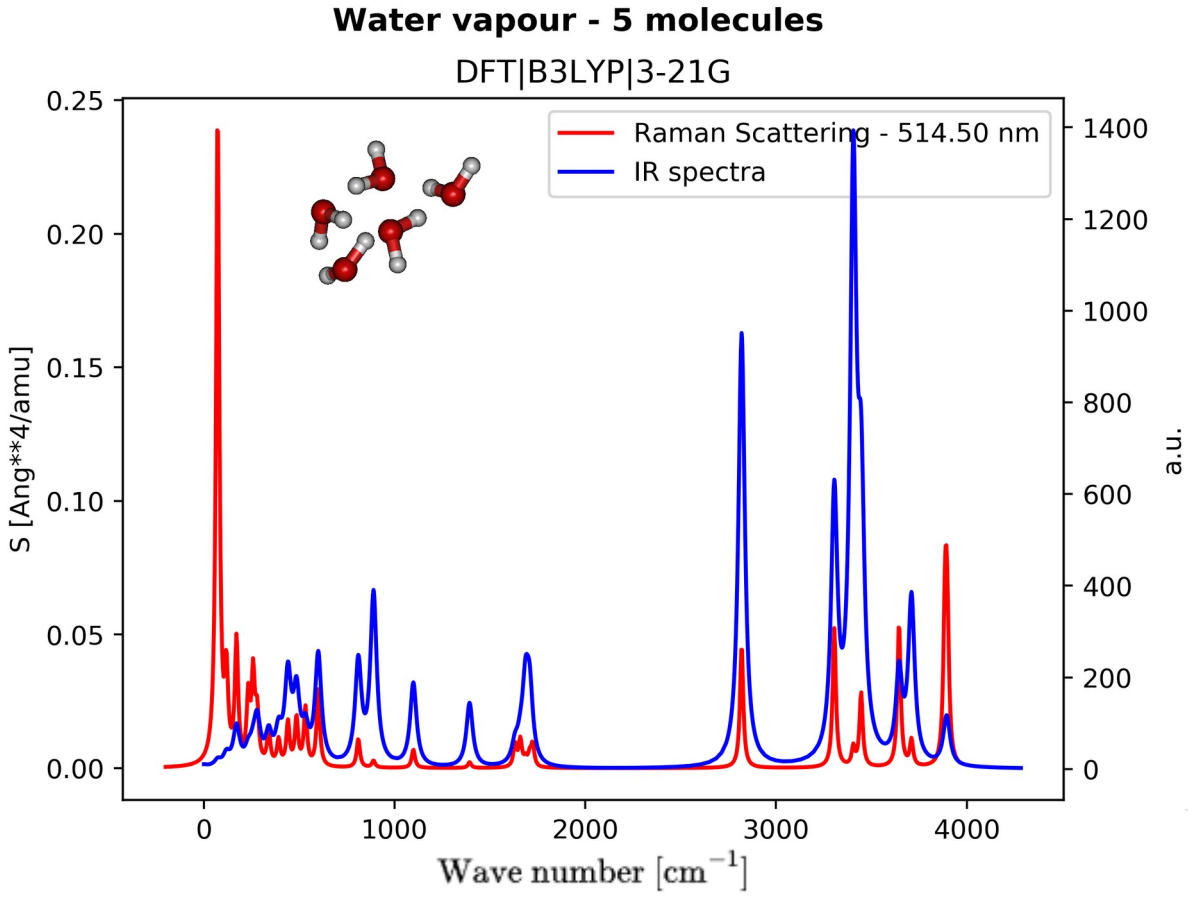
Electronic density



HOMO



LUMO

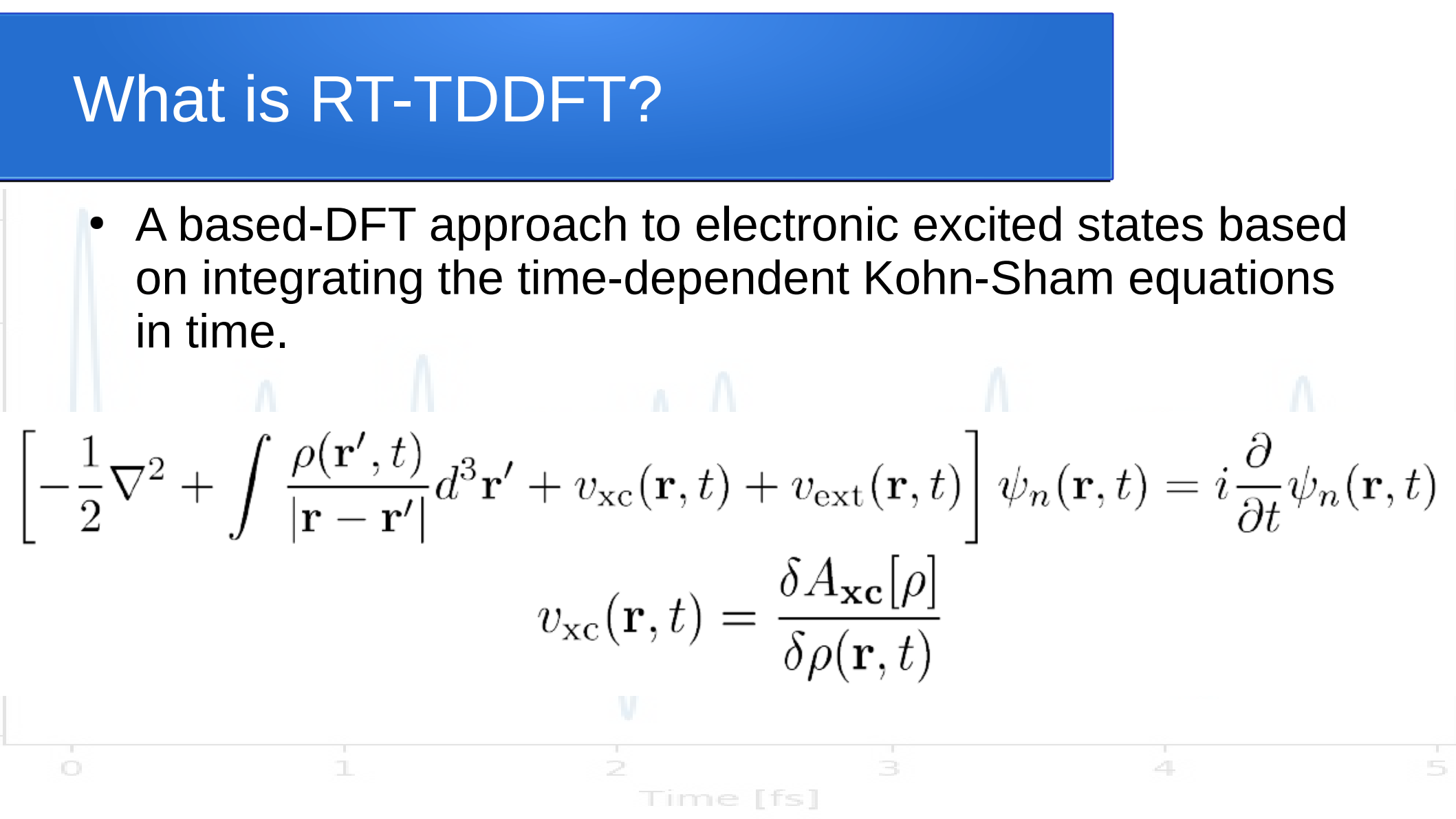


What is RT-TDDFT?

- A based-DFT approach to electronic excited states based on integrating the time-dependent Kohn-Sham equations in time.

$$\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' + v_{\mathrm{xc}}(\mathbf{r},t) + v_{\mathrm{ext}}(\mathbf{r},t)\right]\psi_n(\mathbf{r},t) = i\frac{\partial}{\partial t}\psi_n(\mathbf{r},t)$$

$$v_{\mathrm{xc}}(\mathbf{r},t) = \frac{\delta A_{\mathbf{xc}}[\rho]}{\delta\rho(\mathbf{r},t)}$$



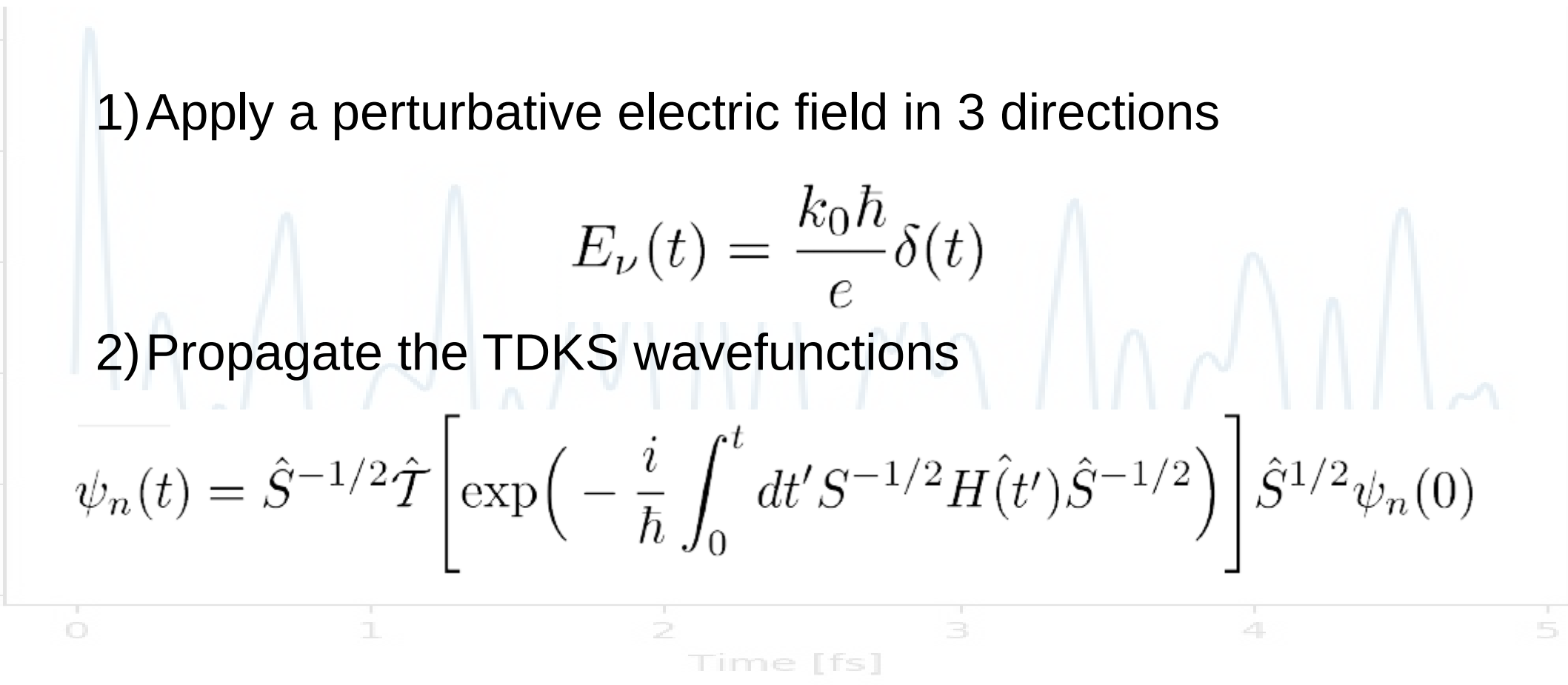
Formalism (steps 1-2)

1) Apply a perturbative electric field in 3 directions

$$E_\nu(t) = \frac{k_0 \hbar}{e} \delta(t)$$

2) Propagate the TDKS wavefunctions

$$\psi_n(t) = \hat{S}^{-1/2} \hat{\mathcal{T}} \left[\exp\left(-\frac{i}{\hbar} \int_0^t dt' S^{-1/2} H(\hat{t}') \hat{S}^{-1/2} \right) \right] \hat{S}^{1/2} \psi_n(0)$$



Formalism (steps 3-4)

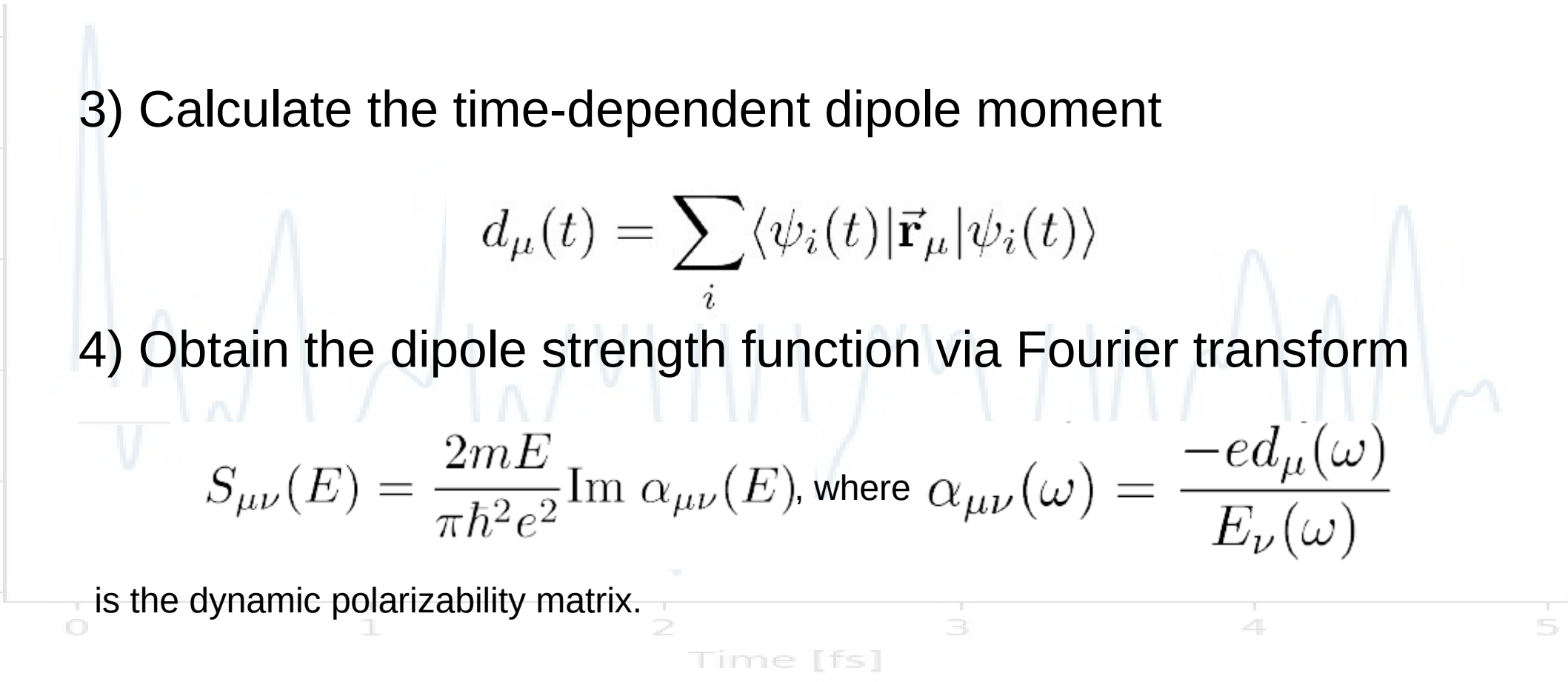
3) Calculate the time-dependent dipole moment

$$d_\mu(t) = \sum_i \langle \psi_i(t) | \vec{\mathbf{r}}_\mu | \psi_i(t) \rangle$$

4) Obtain the dipole strength function via Fourier transform

$$S_{\mu\nu}(E) = \frac{2mE}{\pi\hbar^2 e^2} \mathrm{Im}\ \alpha_{\mu\nu}(E), \text{ where } \alpha_{\mu\nu}(\omega) = \frac{-e d_\mu(\omega)}{E_\nu(\omega)}$$

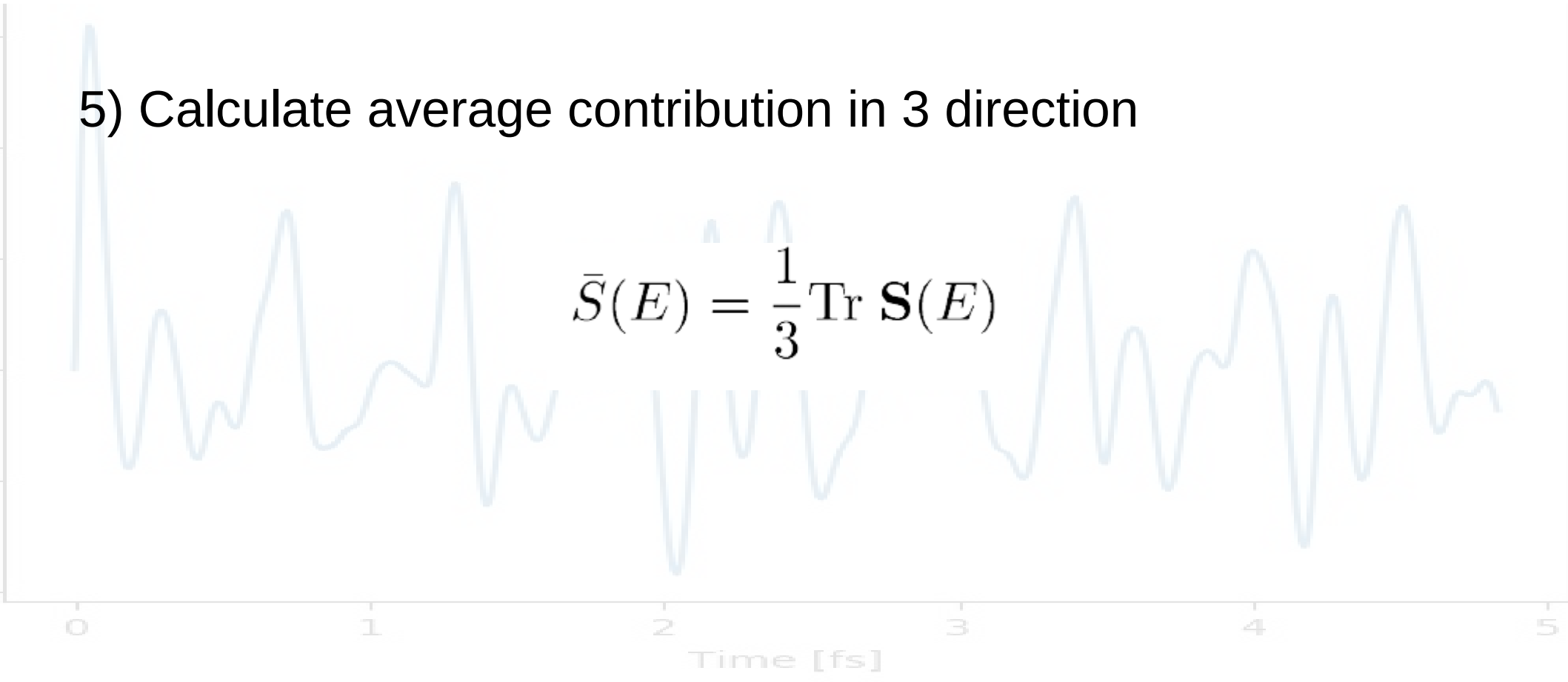
is the dynamic polarizability matrix.



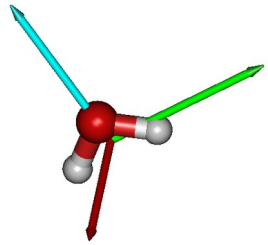
Formalism (steps 5)

5) Calculate average contribution in 3 direction

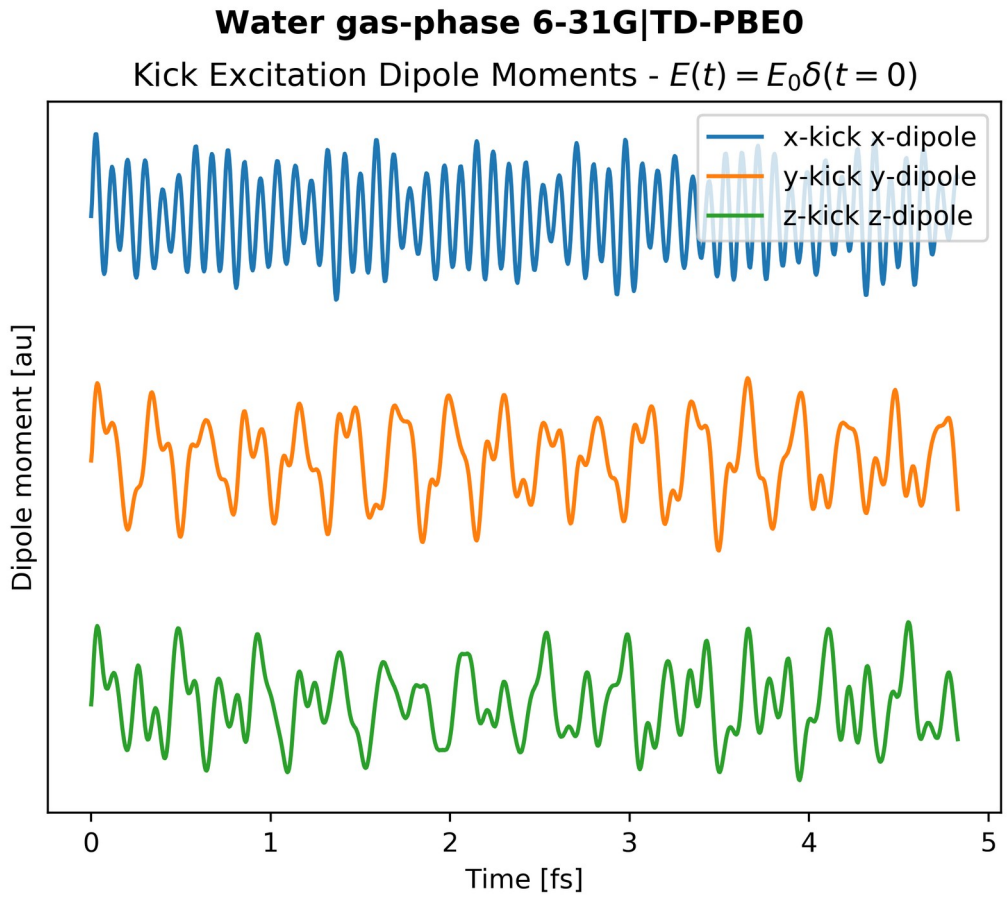
$$\bar{S}(E) = \frac{1}{3}\mathrm{Tr}\ \mathbf{S}(E)$$



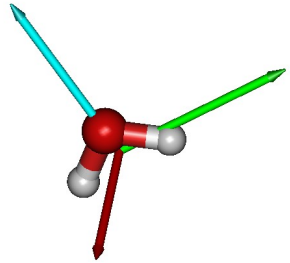
Water gas-phase molecule



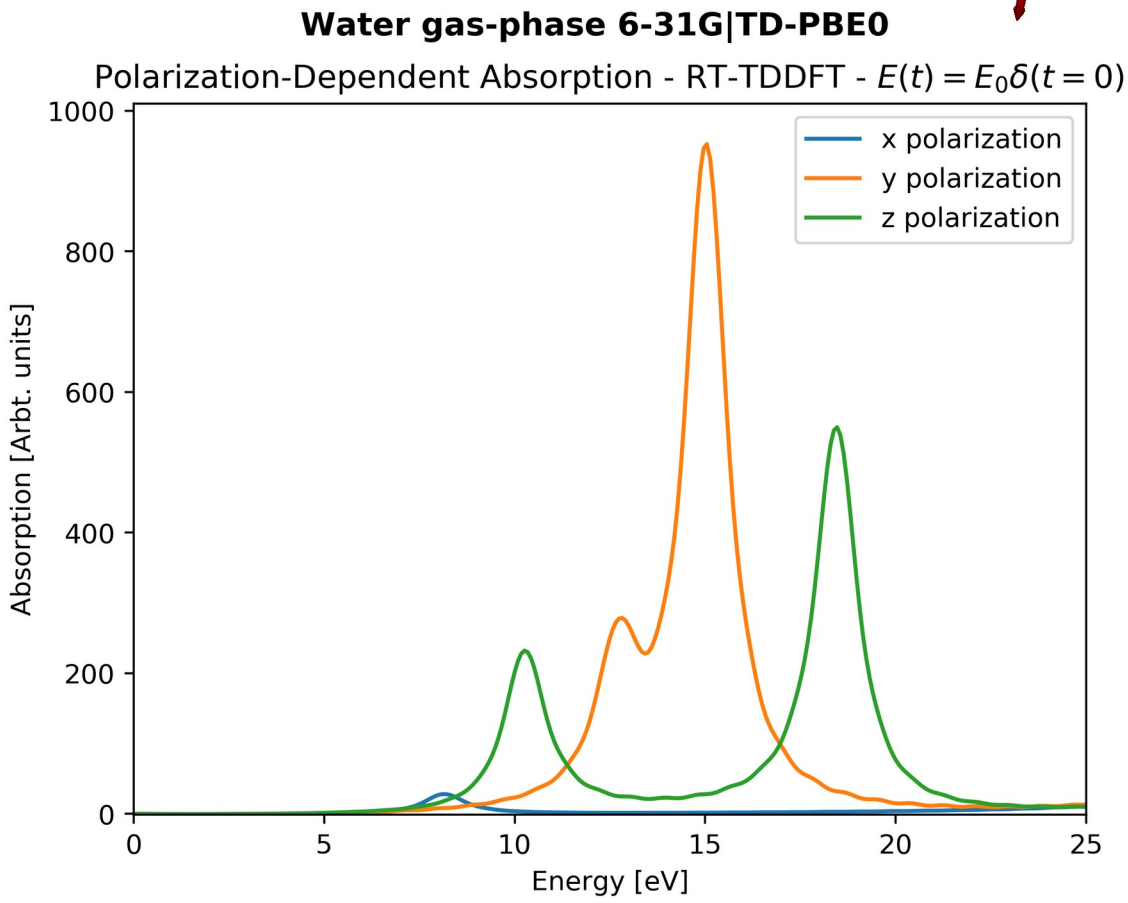
$$d_\mu(t) = \sum_i \langle \psi_i(t) | \vec{\mathbf{r}}_\mu | \psi_i(t) \rangle$$

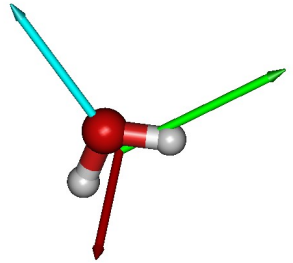


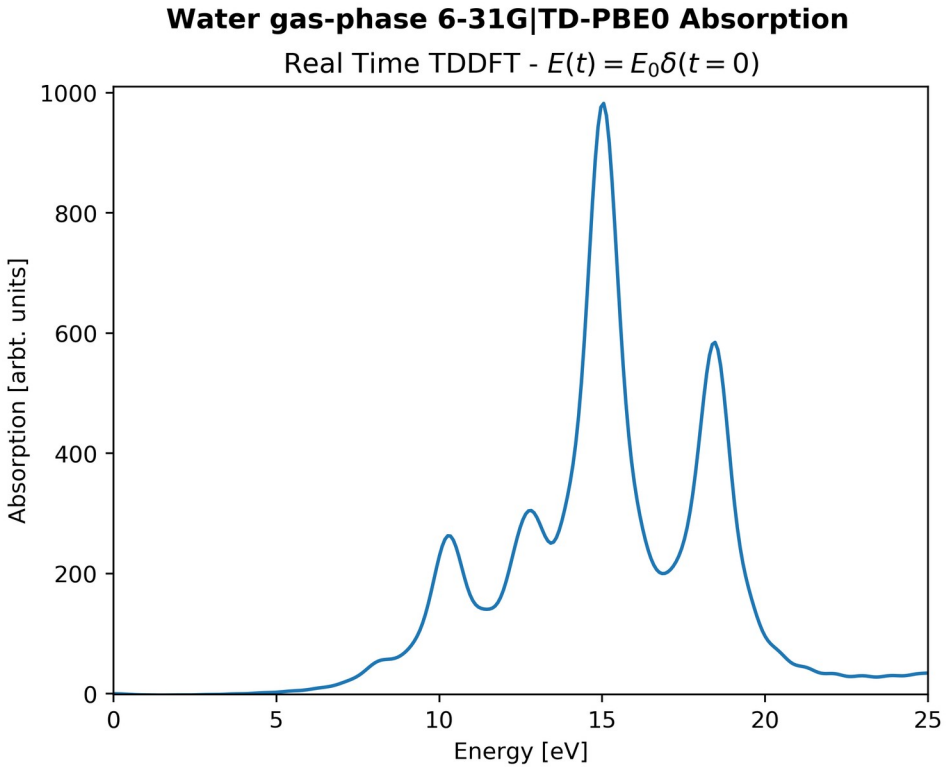
Water gas-phase molecule

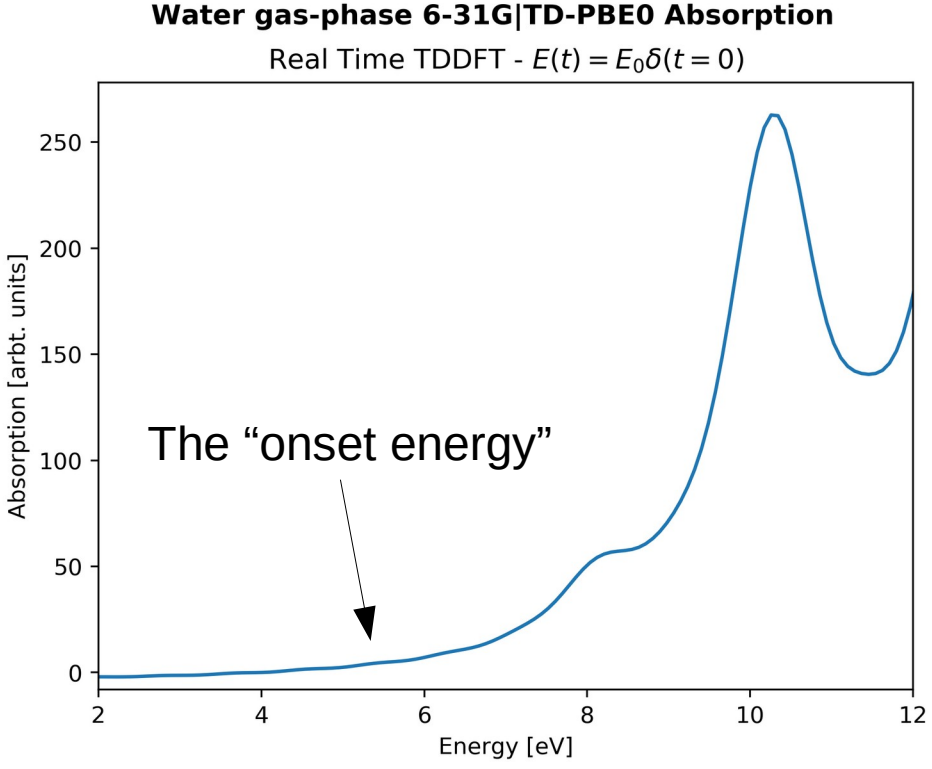


$$S_{\mu\nu}(E) = \frac{2mE}{\pi\hbar^2 e^2}\,\mathrm{Im}\;\alpha_{\mu\nu}(E)$$

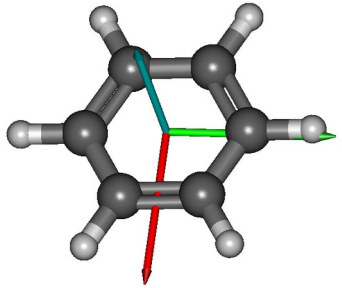


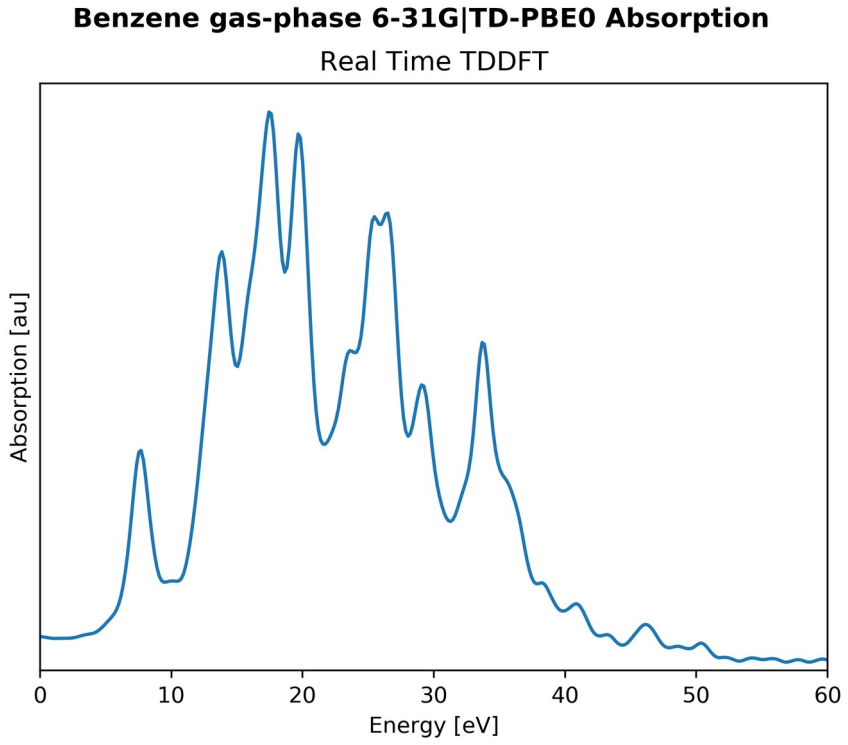


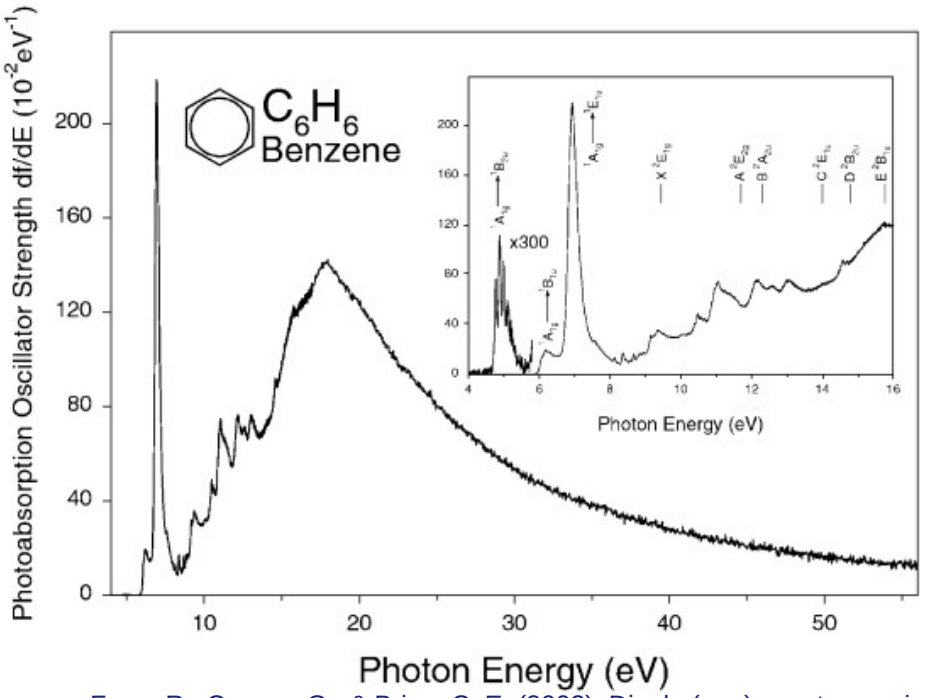

Water gas-phase 6-31G|TD-PBE0 Absorption
Real Time TDDFT - $E(t) = E_0\delta(t = 0)$
Absorption [arbt. units]
Energy [eV]
0
200
400
600
800
1000
0
5
10
15
20
25


Water gas-phase 6-31G|TD-PBE0 Absorption
Real Time TDDFT - $E(t) = E_0\delta(t = 0)$
Absorption [arbt. units]
Energy [eV]
The “onset energy”
0
50
100
150
200
250
2
4
6
8
10
12

Benzene molecule







Feng, R., Cooper, G., & Brion, C. E. (2002). Dipole (e, e) spectroscopic studies of benzene: quantitative photoabsorption in the UV, VUV and soft X-ray regions. Journal of electron spectroscopy and related phenomena, 123(2-3), 199-209.

Softwares

NWChem: Open Source High-Performance Computational Chemistry

EMSL

python™

References

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