Electronic properties

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Tutorial CPMD-CP2K

Observables

Knowledge of $n(\vec{r})$ gives knowledge of $v(\vec{r})$ and of Ψ_0,

thus all properties of the electronic system and in particular any expectation value of an observable $O = \langle\Psi|\hat{O}|\Psi\rangle$, are functionals of $n(\vec{r})$ ($O[n]$ for the observable $\hat{O}$).

If $\hat{O}$

- is a single particule operator
- depends only of the position operator $\hat{\vec{r}}$: $\hat{O} \equiv O(\hat{\vec{r}})$

then $O = \langle\Psi|\hat{O}|\Psi\rangle = \int d^3\vec{r}\, n(\vec{r})O(\vec{r})$

Two and more electron observables

For an observable $\hat{O}$ like $\hat{\vec{M}}^2$ there is no simple expression of $\langle \Psi_0 | \hat{O} | \Psi_0 \rangle$ as a density functional, in particular :

$$\langle \Psi_0 | \hat{\vec{M}}^2 | \Psi_0 \rangle \neq \int n(\vec{r}\,)\vec{r}^{\,2}\, d\vec{r}$$

since

$$\hat{\vec{M}}^2 = \sum_{i,j} \vec{r}_i \cdot \vec{r}_j$$

We can use the Kohn-Sham orbitals as **an approximation** :

$$\langle \Psi_0 | \hat{\vec{M}}^2 | \Psi_0 \rangle \approx \langle \Psi_s | \hat{\vec{M}}^2 | \Psi_s \rangle$$

where Ψ_s is the Slater determinant of the auxiliary non-interacting system associated to n :

$$\Psi_s = \frac{1}{N!} \det[\phi_1 \phi_2 \ldots \phi_N]$$

Response properties

Fortunately in many cases the quantity experimentaly accessible is not $\langle \Psi_0 | \hat{\vec{M}}^2 | \Psi_0 \rangle$ but a response property, in this case that would be the polarizability :

$$\alpha_{ij} = \frac{\partial M_i}{\partial \mathcal{E}_j} = -\frac{\partial^2 E_0}{\partial \mathcal{E}_j \, \partial \mathcal{E}_i}$$

$(\vec{M} = -\dfrac{\partial E_0}{\partial \vec{\mathcal{E}}} = \langle \Psi_0 | \hat{\vec{M}} | \Psi_0 \rangle$: Hellmann-Feynman)

Other response property, the Hessian :

$$-\frac{\partial^2 E_0}{\partial \vec{R}_I \, \partial \vec{R}_J} = \frac{\partial \vec{F}_J}{\partial \vec{R}_I}$$

Finite difference or perturbation theory

Density Functional Response Theory

$$\alpha_{ij} = \frac{\partial M_i}{\partial \mathcal{E}_j} = \frac{\partial}{\partial \mathcal{E}_j} \int d^3\vec{r}\, r_i\, n(\vec{r}\,) = \int d^3\vec{r}\, r_i\, n^{(1)}(\vec{r}\,)$$

where

$$n^{(1)}(\vec{r}\,) = \frac{\partial n(\vec{r}\,)}{\partial \mathcal{E}_j}$$

(in Hessian, supplementary term)
$n^{(1)}(\vec{r}\,)$ can be obtained by Density Functional Perturbation Theory

λ expansion

$$v(\vec{r}) \rightarrow v^{(0)}(\vec{r}) + \lambda v^{(1)}(\vec{r})$$

$$\phi_i(\vec{r}) = \phi_i^{(0)}(\vec{r}) + \lambda \phi_i^{(1)}(\vec{r}) + \lambda^2 \phi_i^{(2)}(\vec{r}) \dots$$
$$n(\vec{r}) = n^{(0)}(\vec{r}) + \lambda n^{(1)}(\vec{r}) + \lambda^2 n^{(2)}(\vec{r}) \dots$$

$$F = E - \Lambda_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right)$$
$$F = F^{(0)} \left(\left\{ \phi_i^{(0)} \right\} \right) + \lambda F^{(1)} \left(\left\{ \phi_i^{(0)} \right\} \right) + \lambda^2 F^{(2)} \left(\left\{ \phi_i^{(0)} \right\}; \left\{ \phi_i^{(1)} \right\} \right) \dots$$

$$\langle \phi_i^{(0)} | \phi_i^{(1)} \rangle + \langle \phi_i^{(1)} | \phi_i^{(0)} \rangle = 0$$

Minimisation in DFPT

Variational principle for the response to a perturbation $v^{(1)}(\vec{r})$:

$$\boxed{\left\{\phi_i^{(1)}\right\} \text{ minimizes } F^{(2)}\left(\left\{\phi_i^{(0)}\right\};\left\{\phi_i^{(1)}\right\}\right)}$$

$$F^{(2)}\left(\left\{\phi_i^{(0)}\right\};\left\{\phi_i^{(1)}\right\}\right) = E^{(2)}\left(\{\phi_i\}\right) - \left(\Lambda_{ij}\left(\langle\phi_i|\phi_j\rangle - \delta_{ij}\right)\right)^{(2)}$$

From

$$F = E - \Lambda_{ij}\left(\langle\phi_i|\phi_j\rangle - \delta_{ij}\right)$$

$$F = \sum_i \langle\phi_i|\frac{1}{2}\nabla^2|\phi_i\rangle + \int d^3\vec{r}\, n(\vec{r})v(\vec{r}) + J[n] + E_{xc}[n]$$
$$- \Lambda_{ij}\left(\langle\phi_i|\phi_j\rangle - \delta_{ij}\right)$$

Taking the second order in the perturbation λ and minimizing with respect to $\left\{\phi_i^{(1)}\right\}$, we obtain that $\left\{\phi_i^{(1)}\right\}$ satisfies the Sternheimer equation :

$$\left(H^{(0)}\delta_{ij} - \Lambda_{ij}^{(0)}\right)\phi_j^{(1)} = \left(H^{(1)}\delta_{ij} - \Lambda_{ij}^{(1)}\right)\phi_j^{(0)}$$

Note that $H^{(1)}$ depends on $n^{(1)}(\vec{r})$

Applications

- Polarizability, Raman spectrum
- phonons
- NMR chemical shifts (use of Wannier orbitals to solve the gauge problem)
- chemical hardness

Response to a static perturbation (stat. mech. aspect)

$$\mathcal{H} = \mathcal{H}_0 - B \cdot X$$

$$\langle A \rangle_X = \langle A \rangle_0 + \frac{\partial \langle A \rangle}{\partial X} \cdot X \ldots +$$

$$= \frac{1}{Z} \frac{1}{N!} \frac{1}{h^{3N}} \int A(\mathbf{q}, \mathbf{p}) e^{-\beta \mathcal{H}(\mathbf{q},\mathbf{p})} \, d\mathbf{q} d\mathbf{p}$$

$$\langle A \rangle_0 = \frac{1}{Z_0} \frac{1}{N!} \frac{1}{h^{3N}} \int A(\mathbf{q}, \mathbf{p}) e^{-\beta \mathcal{H}_0(\mathbf{q},\mathbf{p})} \, d\mathbf{q} d\mathbf{p}$$

$$\frac{\partial \langle A \rangle}{\partial X} = \frac{-\beta}{Z_0} \frac{1}{N!} \frac{1}{h^{3N}} \int A(\mathbf{q}, \mathbf{p}) \frac{\partial \mathcal{H}}{\partial X} e^{-\beta \mathcal{H}_0(\mathbf{q},\mathbf{p})} \, d\mathbf{q} d\mathbf{p} - \frac{1}{Z_0^2} \frac{\partial Z_0}{\partial X} \cdot \frac{1}{N!} \frac{1}{h^{3N}} \int A(\mathbf{q}, \mathbf{p}) e^{-\beta \mathcal{H}_0(\mathbf{q},\mathbf{p})} \, d\mathbf{q} d\mathbf{p}$$

$$\frac{\partial \langle A \rangle}{\partial X} = \beta \langle AB \rangle_0 - \beta \langle B \rangle_0 \langle A \rangle_0$$

response of A proportional to the correlation $\langle AB \rangle_0 - \beta \langle B \rangle_0 \langle A \rangle_0$

Dielectric constant : $A = B \equiv \vec{M}(\vec{q}, \vec{\mathcal{E}})$

$$\chi = \frac{1}{V} \frac{\partial \langle \vec{M} \rangle}{\partial \vec{\mathcal{E}}} = \frac{1}{V} \langle \alpha \rangle_0 + \frac{\beta}{3V} \langle \vec{M} \cdot \vec{M} \rangle_0$$

Note : in *ab initio* MD this is hard to compute (long time correlations) however a good estimate can be obtained by **finite difference** (MD in a finite electric field)

Time-dependent linear response (nuclei)

$$\mathcal{H}(t) = \mathcal{H}_0 - B \cdot X(t)$$

In the linear response regime :

$$\langle A \rangle(t) = \langle A \rangle_0 + \int_{-\infty}^{t} \chi_{AB}(t-\tau) \cdot X(\tau) \, d\tau$$

$\chi_{AB}(t)$ defined for $t > 0$, response to a Dirac pulse $X(t) \equiv \delta(t)$

Useful to take the Fourier transforms

$$\tilde{X}(\omega) = \int_{-\infty}^{+\infty} X(t) e^{-i\omega t}$$

$$\tilde{A}(\omega) = \int_{-\infty}^{+\infty} \langle A \rangle (t) e^{-i\omega t}$$

Then

$$\tilde{A}(\omega) = \tilde{\chi}_{AB}(\omega) \cdot \tilde{X}(\omega)$$

With

$$\tilde{\chi}_{AB}(\omega) = \int_{0}^{+\infty} \chi_{AB}(t) e^{-i\omega t}$$

$\tilde{\chi}_{AB}(\omega)$ frequency dependent susceptibility
Note : $\tilde{\chi}_{AB}(\omega)$ has a real and an imaginary part (related by the dispersion or Kramers-Krönig relations)

Expression for $\chi_{AB}(t)$

perturbation : $-\lambda B \cdot \delta(t)$
$A \equiv A(\vec{R}_I)$, $B \equiv B(\vec{R}_I)$

$$\langle A \rangle(t) = \int d\vec{R}_I d\vec{V}_I \, A(\vec{R}_I(t)) f(\vec{R}_I, \vec{V}_I)$$

$$m_I \frac{d\vec{V}_I}{dt} = \vec{F}_I^0 + \lambda \frac{\partial B}{\partial \vec{R}_I} \delta(t)$$

$$m_I \vec{V}_I(t = 0^+) = m_I \vec{V}_I(t = 0^-) + \lambda \frac{\partial B}{\partial \vec{R}_I}$$

$$f(\vec{R}_I, \vec{V}_I; t = 0^+) = f(\vec{R}_I, \vec{V}_I - \lambda \frac{1}{m_I} \frac{\partial B}{\partial \vec{R}_I}; t = 0^-)$$

$$= \frac{1}{Z_0} e^{-\beta V_0(\vec{R}_I)} \exp\left[-\beta \frac{m_I(\vec{V}_I - \lambda \frac{1}{m_I} \frac{\partial B}{\partial \vec{R}_I})^2}{2} \right]$$

$$f(\vec{R}_I, \vec{V}_I; t = 0^+) \approx \frac{1}{Z_0} e^{-\beta V_0(\vec{R}_I)} \exp\left(-\beta \frac{m_I \vec{V}_I^2}{2}\right) \times \left(1 + \beta\lambda \vec{V}_I \frac{\partial B}{\partial \vec{R}_I}\right)$$

$$\begin{aligned} \langle A\rangle(t) - \langle A\rangle &= \frac{\beta\lambda}{Z_0} \int d\vec{R}_I d\vec{V}_I \left(\vec{V}_I \frac{\partial B}{\partial \vec{R}_I}\right) A(\vec{R}_I(t)) e^{-\beta V_0(\vec{R}_I)} e^{-\beta \frac{m_I \vec{V}_I^2}{2}} \\ &= \frac{\beta\lambda}{Z_0} \int d\vec{R}_I d\vec{V}_I \frac{\partial B(\vec{R}_I)}{\partial t} A(\vec{R}_I(t)) e^{-\beta V_0(\vec{R}_I)} e^{-\beta \frac{m_I \vec{V}_I^2}{2}} \end{aligned}$$

The susceptibility is then

$$\boxed{\frac{\langle A\rangle(t) - \langle A\rangle_0}{\lambda} \equiv \chi_{AB}(t) = \beta\langle\frac{\partial B}{\partial t}(0)A(t)\rangle_0}$$

It is determined by time correlations of the unperturbed system.

more general demonstration see e.g. :
R. Kubo et al. *Statistical Physics II – Nonequilibrium Statistical Mechanics* (Springer Verlag, Berlin, 1991)

Infrared spectroscopy

An oscillating electric field along z is applied on the system :
$\mathcal{E}_z(t) = \mathcal{E}_0 \cos \omega_0 t$ or more generally

$$\mathcal{E}_z(t) = \frac{1}{2\pi} \int d\omega \tilde{\mathcal{E}}_z(\omega) e^{i\omega t}$$

The perturbation is then $-M_z \cdot \mathcal{E}_z(t)$
The energy dissipated per unit volume is

$$U = \int dt \, j_z(t) \cdot \mathcal{E}_z(t)$$

with the current per unit volume $j_z(t) = \frac{1}{V} \frac{dM_z}{dt}(t)$ (Joule's law)

$$j_z(t) = \frac{\beta}{V} \int_{-\infty}^{t} \langle \dot{M}_z(0) \dot{M}_z(t-\tau) \rangle_0 \cdot \mathcal{E}_z(\tau) \, d\tau$$

Parseval relation :

$$\int dt\, j_z(t) \cdot \mathcal{E}_z(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega\, \tilde{j}_z(\omega) \tilde{\mathcal{E}}_z^*(\omega)$$

$$\tilde{j}_z(\omega) = \tilde{\chi}_{zz}(\omega) \tilde{\mathcal{E}}_z(\omega)$$

with

$$\tilde{\chi}(\omega) = \frac{\beta}{V} \int_0^{+\infty} e^{-i\omega t} \langle \dot{M}_z(0) \dot{M}_z(t) \rangle_0$$

then

$$U = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega\, \tilde{\chi}_{zz}(\omega) \left| \tilde{\mathcal{E}}_z(\omega) \tilde{\mathcal{E}}_z^*(\omega) \right|$$

since $\mathcal{E}_z(t)$ is real, $\tilde{\mathcal{E}}_z(-\omega) = \tilde{\mathcal{E}}_z^*(\omega)$
and

$$U = \frac{1}{2\pi} \int_0^{+\infty} d\omega \; \left(\tilde{\chi}_{zz}(\omega) + \tilde{\chi}_{zz}(-\omega)\right) \left|\tilde{\mathcal{E}}_z(\omega)\tilde{\mathcal{E}}_z^*(\omega)\right|$$

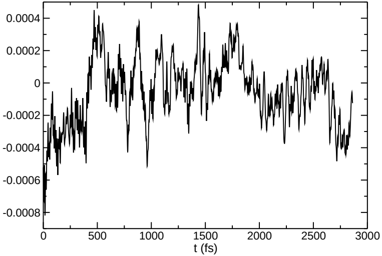
$$\begin{aligned} \tilde{\chi}_{zz}(\omega) + \tilde{\chi}_{zz}(-\omega) &= \frac{\beta}{V} \int_{-\infty}^{+\infty} e^{-i\omega t} \langle \dot{M}_z(0)\dot{M}_z(t)\rangle_0 \\ &= \frac{\beta}{V}\omega^2 \int_{-\infty}^{+\infty} e^{-i\omega t} \langle M_z(0)M_z(t)\rangle_0 \end{aligned}$$

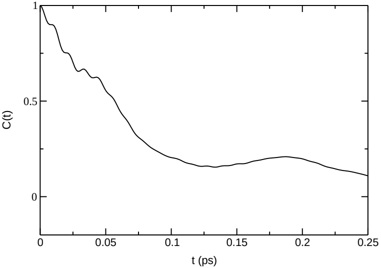
Finally,

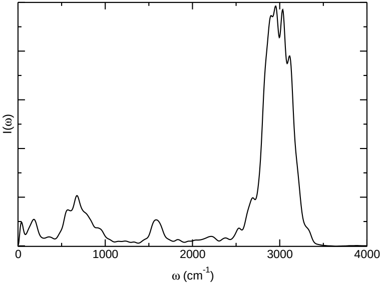
$$\boxed{I_{IR}(\omega) \propto \frac{\beta}{V}\omega^2 \int_{-\infty}^{+\infty} e^{-i\omega t} \langle M_z(0)M_z(t)\rangle_0}$$

One special instance of the fluctuation-dissipation theorem

Example : infrared spectrum of water







$$I(\omega) = \frac{\beta\omega^2}{2} \int_{-\infty}^{\infty} e^{i\omega t} \langle M(0)M(t)\rangle_0 dt$$