Calculating the dielectric constant within QMC

Richard Needs

Theory of Condensed Matter Group
Cavendish Laboratory
University of Cambridge

The macroscopic polarisation

The macroscopic polarisation $\mathbf{P}$ of a finite system is

$$\mathbf{P} = \frac{1}{\Omega}\int_{\Omega} \mathcal{P}(\mathbf{r})\, d^3r = \frac{1}{\Omega}\int_{\Omega} \mathbf{r}\,\rho(\mathbf{r})\, d^3r$$

$\mathcal{P}(\mathbf{r}) \equiv$ polarisation density
$\rho(\mathbf{r}) \equiv$ total charge density

Within periodic boundary conditions it is more difficult to define $\mathbf{P}$
Choosing different unit cells → different values for the integral

Within the Berry phase formalism of King-Smith, Vanderbilt, and Resta:

$$\begin{aligned} P[\Psi] &= -\frac{1}{\Omega}\frac{L}{2\pi}\,\mathrm{Im}\ln z \\ z &= \left\langle \Psi \left| e^{i\frac{2\pi}{L}\sum_i^N x_i} \right| \Psi \right\rangle \end{aligned}$$

$L \equiv$ Length of simulation cell

The static dielectric constant

Static dielectric constant

$$\begin{aligned} \epsilon_0 &= 1 + 4\pi \frac{\partial P}{\partial \mathcal{E}} \\ &= 1 + 4\pi\chi \end{aligned}$$

$\chi \equiv$ polarisability
The differential with respect to applied electric field $\mathcal{E}$

Can use DFT to calculate P
Can use Density Functional Perturbation Theory (DFPT) to calculate ϵ_0

DFT is normally quite accurate for P but less accurate for ϵ_0
Typically off by $\sim 20\%$, but sometimes worse

The static dielectric constant in QMC

Umari, Williamson, Galli, and Marzari (using CASINO!)

Finite applied electric field $\mathcal{E}$: consider electric enthalpy F

$$F = \langle\Psi|\hat{H}|\Psi\rangle - \Omega P[\Psi]\mathcal{E}$$

Minimising with respect to $|\Psi\rangle$

$$\frac{\partial F}{\partial\langle\Psi|} = \lambda|\Psi\rangle$$

find that $|\Psi\rangle$ is the ground state of an effective Hamiltonian

$$\hat{H}_{\text{eff}} = \hat{H} + \mathcal{E}\frac{L}{2\pi}\,\text{Im}\left[\frac{e^{i2\pi/L\,\sum_i x_i}}{\langle\Psi|e^{i2\pi/L\,\sum_i x_i}|\Psi\rangle}\right]$$

$\hat{H}_{\text{eff}}$ is periodic, local, real, and Hermitian, but depends on Ψ
$\longrightarrow$ iterate to self-consistency

QMC calculations of Umari *et al.*

1D chain of H_2 molecules subject to periodic boundary conditions
Local H pseudopotential
Slater determinant of PBE-GGA orbitals + (bad) Jastrow factor
Simulation cells with up to 22 H_2 molecules
Electric field of 0.001 a.u.
Polarisability by finite difference method

Method	χ (a.u.)	Scaling cost
PBE-GGA	144.5	$N - N^3$
CCD	47.6	$N^5 - N^6$
CCSD	48.0	N^6
CCSD(T)	50.6	N^7
MP2	58.0	N^5
MP3	54.3	N^6
MP4	53.6	N^7
DMC	53.4(11)	$N - N^3$

Table 1: Linear polarisability per H_2 unit for a periodic linear chain of H_2 dimers calculated using several methods, together with their associated scaling costs. The quantum chemistry results are from PRA **52** 1039 (1995).

Kohn formulation

Really interested in the case of a vanishingly small electric field

Kohn, Phys. Rev. **105**, 509 (1957)
Kohn, Phys. Rev. **110**, 857 (1958)

$$\frac{1}{\epsilon_0} = \lim_{\substack{\mathbf{K},\mathbf{K}'\to 0 \\ \mathbf{K}\neq\mathbf{K}'}} \frac{\langle \Psi_{0\mathbf{K}'} | \rho_{\mathbf{K}-\mathbf{K}'} | \Psi_{0\mathbf{K}} \rangle}{\langle \Psi_{0\mathbf{K}'} | \Psi_{0\mathbf{K}} \rangle}$$

$$\text{where} \quad \rho_{\mathbf{K}}(\mathbf{r}) = \sum_{i=1}^{N} e^{i\mathbf{K}.\mathbf{r}}$$

But.........what does the limit mean?

Conclusions

- Work of Umari *et al.* is very nice
- Can anybody understand the Kohn equation?
- Nice to try the Kohn equation (providing we can understand it!)