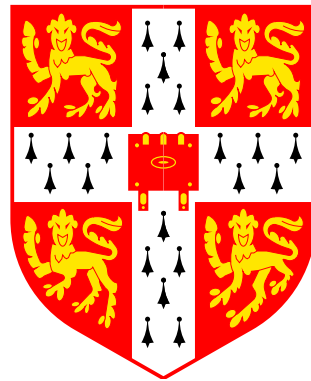


# Calculating the dielectric constant within QMC

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# 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  $\rightarrow$  different values for the integral

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

$$P[\Psi] = -\frac{1}{\Omega} \frac{L}{2\pi} \text{Im} \ln z$$
$$z = \langle \Psi | e^{i\frac{2\pi}{L} \sum_i^N x_i} | \Psi \rangle$$

$L \equiv$  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  $\epsilon_0$

DFT is normally quite accurate for  $P$  but less accurate for  $\epsilon_0$

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  $\Psi$   
→ iterate to self-consistency

# QMC calculations of Umari *et al.*

1D chain of H<sub>2</sub> 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<sub>2</sub> molecules

Electric field of 0.001 a.u.

Polarisability by finite difference method

Method	$\chi$ (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<sub>2</sub> unit for a periodic linear chain of H<sub>2</sub> 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)

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

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

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!)