Density functional perturbation theory

Extending the Hamiltonian

- A *virtual* experiment ... Definition of experiment: perturb given system and observe response $\longrightarrow$ increased understanding.

  1 Include perturbation in Hamiltonian, *i.e.* additional external potential.

  2 Get electronic structure *via* variational principle.

  3 Consider how expectation values change.

$\longrightarrow$ perturbational Hamiltonian defines the problem as an external field.

- appealing concept to scientists: experiment, expansion, well defined perturbation.

Perturbation Theory - fundamental

- Taylor-expansion of $\widehat{H}$, Ψ_j, and E_j,

$$\begin{aligned}\widehat{H} &= \widehat{H}^{(0)} + \lambda \widehat{H}^{(1)} + ... \\ \Psi_j &= \Psi_j^{(0)} + \lambda \Psi_j^{(1)} + ... \\ E_j &= E_j^{(0)} + \lambda E_j^{(1)} + ...\end{aligned}$$

- Assume that expansion converges and perturbation be small

- Schrödinger equation,

$$\left[\widehat{H}^{(0)} + \lambda \widehat{H}^{(1)} + ...\right] \left[\Psi_j^{(0)} + \lambda \Psi_j^{(1)} + ...\right] = \left[\Psi_j^{(0)} + \lambda \Psi_j^{(1)} + ...\right] \left[E_j^{(0)} + \lambda E_j^{(1)} + ...\right]$$

Perturbation Theory - fundamental

- Order according to λ,

$$
\begin{aligned}
0 \;=\;& \left(\widehat{H}^{(0)} - E_j^{(0)}\right)\Psi_j^{(0)} \\
&+\lambda\left[\left(\widehat{H}^{(1)} - E_j^{(1)}\right)\Psi_j^{(0)} + \left((\widehat{H}^{(0)} - E_j^{(0)}\right)\Psi_j^{(1)}\right] \\
&+\ldots
\end{aligned}
$$

$\rightarrow$ coefficients of λ of any order must vanish,

$$
\begin{aligned}
0 &= \left(\widehat{H}^{(0)} - E_j^{(0)}\right)\Psi_j^{(0)} \\
0 &= \left[\left(\widehat{H}^{(1)} - E_j^{(1)}\right)\Psi_j^{(0)} + \left((\widehat{H}^{(0)} - E_j^{(0)}\right)\Psi_j^{(1)}\right] \\
0 &= \ldots
\end{aligned}
$$

Perturbation Theory - $E^{(1)}$

- Consider the unperturbed wavefunction to be already optimized,

$$\begin{aligned}
0 &= \left(\widehat{H}^{(1)} - E_j^{(1)}\right)\Psi_j^{(0)} + \left((\widehat{H}^{(0)} - E_j^{(0)}\right)\Psi_j^{(1)} \\
0 &= \langle\Psi_j^{(0)}|\left(\widehat{H}^{(1)} - E_j^{(1)}\right)|\Psi_j^{(0)}\rangle + \langle\Psi_j^{(0)}|\left((\widehat{H}^{(0)} - E_j^{(0)}\right)|\Psi_j^{(1)}\rangle \\
0 &= \langle\Psi_j^{(0)}|\left(\widehat{H}^{(1)} - E_j^{(1)}\right)|\Psi_j^{(0)}\rangle \\
E_j^{(1)} &= \langle\Psi_j^{(0)}|\widehat{H}^{(1)}|\Psi_j^{(0)}\rangle
\end{aligned}$$

- First order energy perturbation is simply ground state expectation value of perturbational Hamiltonian, *i.e.* in DFT,

$$E^{(1)} = \int_{\mathbf{r}} n(\mathbf{r})\,\widehat{H}^{(1)}\,d\mathbf{r} \approx \partial_{v_{\text{ext}}} E^{(0)}$$

Perturbation Theory - $\Psi_j^{(1)}$

- Expand perturbed wavefunction in a basis of unperturbed wavefunctions

$$\Psi_j^{(1)} = \sum_{i \neq j} c_{ij} \Psi_i^{(0)}$$

- Hence

$$\begin{aligned}
0 &= \left(\widehat{H}^{(1)} - E_j^{(1)}\right) \Psi_j^{(0)} + \left(\widehat{H}^{(0)} - E_j^{(0)}\right) \Psi_j^{(1)} \\
0 &= \langle \Psi_k^{(0)} | \left(\widehat{H}^{(1)} - E_j^{(1)}\right) | \Psi_j^{(0)} \rangle + \sum_{i \neq j} c_{ij} \langle \Psi_k^{(0)} | \left((\widehat{H}^{(0)} - E_j^{(0)}\right) | \Psi_i^{(0)} \rangle \\
0 &= \langle \Psi_k^{(0)} | \widehat{H}^{(1)} | \Psi_j^{(0)} \rangle - c_{kj} (E_k^{(0)} - E_j^{(0)}) \\
c_{kj} &= \frac{\langle \Psi_k^{(0)} | \widehat{H}^{(1)} | \Psi_j^{(0)} \rangle}{E_k^{(0)} - E_j^{(0)}}
\end{aligned}$$

Apply to DFT - DFPT

Expansion of the perturbation

$$
\begin{aligned}
E[n] &= E^{(0)}[n^{(0)}] + \lambda E^{(1)}[n^{(0)}] + \frac{1}{2}\lambda^2 E^{(2)}[n^{(1)}]... \\
\phi &= \phi^{(0)} + \lambda\phi^{(1)} + ... \\
n(\mathbf{r}) &= \sum_i |\phi_i^{(0)} + \phi_i^{(1)} + ...|^2 \\
n(\mathbf{r}) &= \sum_i \left(|\phi_i^{(0)}|^2 + \left(\phi_i^{*(0)}\phi_i^{(1)} + \phi_i^{*(1)}\phi_i^{(0)}\right) + ...\right)
\end{aligned}
$$

Integrated perturbation must be zero:

$$
\begin{aligned}
\int d\mathbf{r}\; n^{(1)} &= 0 \\
\rightarrow \langle\phi_i^{(0)}|\phi_i^{(1)}\rangle + \langle\phi_i^{(1)}|\phi_i^{(0)}\rangle &= 0 \;\forall\; i \\
\rightarrow \langle\phi_i^{(0)}|\phi_j^{(1)}\rangle &= 0 \;\forall\; i,j \qquad (1)
\end{aligned}
$$

Apply to DFT - DFPT

unperturbed ϕ are known, go variational

$$
\begin{aligned}
\min_{\{\phi\}} E[\{\phi\}] \quad &\leftrightarrow \quad \min_{\{\phi_i^{(1)}\}} E^{(2)}[\{\phi^{(0)}, \phi^{(1)}\}] \\
E^{(2)} \quad &= \quad \phi^{*(1)} \frac{\delta^2 E^{(0)}}{\delta\phi^*\delta\phi} \phi^{(1)} + \frac{\delta E^{(1)}}{\delta\phi} \phi^{(1)} \\
\text{orthogonality: } \langle \phi_j^{(0)} | \phi_k^{(1)} \rangle \quad &= \quad 0 \quad \forall \; j, k
\end{aligned} \tag{2}
$$

Second order — already only XC contribution left. Self-consistent response:

$$
\delta V_{\mathrm{SCF}}(\mathbf{r}, \pm\omega) = \int \left\{ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \left. \frac{\delta^2 E_{\mathrm{XC}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \right|_{n^{\{0\}}} \right\} n^{\{1\}}(\mathbf{r}', \pm\omega) \; d\mathbf{r}'
$$

SCF calculation

Iterative calculation

$$\left(\hat{H}^{(0)}\delta_{ij} - \epsilon_{ij}^{(0)}\right)\phi_j^{(1)} + \hat{H}^{(3)}[n^{(1)}] = -\hat{H}^{(1)}\phi_i^{(0)} \tag{3}$$

There is the formal solution

$$\phi_i^{(1)} = \hat{G}_{ij}\hat{H}^{(1)}\phi_j^{(0)} \tag{4}$$

More details in [*J. Phys. Chem. A* **105**, 1951 (2001), *J. Chem. Phys.* **113**, 7102 (2000).]

Applications of DFPT

Phonons, Raman (polarisability), NMR, . . .

Kohn-Sham DFT - a refreshment

Electronic density, total energy functional, *ab initio*

$$
\begin{aligned}
E_{KS} &= -\frac{1}{2}\sum_i \langle\phi_i|\nabla^2|\phi_i\rangle \\
&\quad +\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{\mathbf{r}-\mathbf{r}'} \\
&\quad -\sum_I Z_I \int d\mathbf{r}\frac{n(\mathbf{r})}{\mathbf{r}-\mathbf{R}_I} \\
&\quad +E_{xc} \\
n(\mathbf{r}) &= \sum_i |\phi_i(\mathbf{r})|^2
\end{aligned}
$$

Introducing the KS-orbitals

Ansatz:

- Assume one electron orbitals $\{\phi_i\}$ which are multiplicative in their Slater determinant wave function (*i. e.* non-interacting),

$$\Psi_s = \frac{1}{N!} \, | \, \phi_1 \, \phi_2 \ldots \phi_N \, |.$$

- And that orbitals ϕ_i are eigenstates of an effective yet undefined (Kohn-Sham) potential v_s and orthonormal,

$$\widehat{H}_s \phi_i = \epsilon_i \phi_i \qquad \widehat{H}_s = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r})$$

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \qquad n(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2$$

Kohn-Sham scheme: Total energy

- This *Ansatz* leads to the total energy

$$E_{\mathrm{KS}}[n] = \int_{\mathbf{r}} n(\mathbf{r})\, v_{\mathrm{ext}}(\mathbf{r})\, d\mathbf{r} + T_s[n] + E_H[n] + E_{xc}[n]$$

  or,

$$E[n] = \int_{\mathbf{r}} n(\mathbf{r})\, v_{\mathrm{ext}}(\mathbf{r})\, d\mathbf{r} + F_{\mathrm{universal}}[n].$$

- The first term corresponds to interaction between electrons and external potential (ionic density + perturbations), and

$$\begin{aligned} T_s &= -\frac{1}{2} \min_{\{\phi_i\} \mapsto n} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle; \ \text{kinetic energy of non} - \text{interactingelectrons} \\ E_H[n] &= \frac{1}{2} \int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'\, d\mathbf{r}; \ \text{the classical Coulomb interaction, or Hartree term} \\ E_{xc}[n]; &\quad \text{all the remainder, } \textit{i. e.} \\ E_{xc}[n] &= (T[n] - T_s[n]) + (E_{ee} - E_H[n]) \end{aligned}$$

Kohn-Sham potential

How to know the potential for KS-orbitals?

- Use variational principle: for infinitesimally small variation $\delta n(\mathbf{r})$ (conserving N, *i. e.* $\int_{\mathbf{r}} \delta n(\mathbf{r})\, d\mathbf{r} = 0$),

$$\delta E_v = \delta T_s + \int_{\mathbf{r}} \left(v_{\text{ext}}(\mathbf{r}) + \frac{\delta E_H}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right) \delta n(\mathbf{r})\, d\mathbf{r} = 0$$

- At the minimum

$$v_H(\mathbf{r}) = \frac{\delta E_H}{\delta n(\mathbf{r}')} = \int_{\mathbf{r}'} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'; \text{ Hartree potential}$$

$$v_{xc} \equiv \frac{\delta E_{xc}}{\delta n(\mathbf{r})}; \text{ exchange-correlation potential}$$

- But what about the variation of the kinetic energy part, δT_s?

Kohn-Sham potential

Kinetic part δT_s?

- Use HK theorems: associate to n_{NI} unique potential $v_s[n]$ (HK1) and minimise its energy functional E_s (HK2),

$$E_s[n] = \sum_i \langle \phi_i | -\frac{1}{2}\nabla^2 + v_s[n] | \phi_i \rangle = T_s[n] + \int_{\mathbf{r}} v_s(\mathbf{r}, [n])\, n(\mathbf{r})\, d\mathbf{r}$$

  and variationally,

$$\delta E_s = \delta T_s + \int_{\mathbf{r}} v_s(\mathbf{r})\, \delta n(\mathbf{r})\, d\mathbf{r} = 0 \ .$$

- Hence

$$\delta T_s = -\int_{\mathbf{r}} v_s(\mathbf{r})\, \delta n(\mathbf{r})\, d\mathbf{r}$$

Kohn-Sham potential

- Replace δT_s,

$$\delta E_v = -\int_{\mathbf{r}} v_s(\mathbf{r})\,\delta n(\mathbf{r})\,d\mathbf{r} + \int_{\mathbf{r}} \left(v_{\text{ext}}(\mathbf{r}) + \frac{\delta E_H}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right) \delta n(\mathbf{r})\,d\mathbf{r} = 0.$$

- The condition for n to be n_0, *i. e.* the density which minimizes E_v, is that the integrands equate,

$$v_s[n_0](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int_{\mathbf{r}'} \frac{n_0\,(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + v_{xc}[n_0](\mathbf{r})$$

A *self-consistent* evaluation for n_0 is required

- Hohenberg-Kohn theorem: The densities have to become the same

$$n_0(\mathbf{r}) = n_{\text{NI}}\left[v_s(\mathbf{r},[n_0])\right](\mathbf{r}) = n_{\text{NI}}\left[v_{\text{ext}}(\mathbf{r}) + \int_{\mathbf{r}'} \frac{n_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + v_{xc}[n_0](\mathbf{r}) \right](\mathbf{r}) \quad .$$

Ground state energy

Alternative expression

- $E_0 = E_v[n_0]$ is given by

$$E_0 = \int_{\mathbf{r}} v_{\text{ext}}\, n_0 \, d\mathbf{r} + T_s[n_0] + E_H[n_0] + E_{xc}[n_0]$$

- While also,

$$E_s[n_0] = T_s[n_0] + \int_{\mathbf{r}} v_s[n_0]\, n_0 \, d\mathbf{r} = \sum_i^N \epsilon_i$$

Ground state energy

Alternative expression

$$
\begin{aligned}
E_0 &= \int_{\mathbf{r}} v_{\text{ext}}\, n_0\, d\mathbf{r} + T_s[n_0] + E_H[n_0] + E_{xc}[n_0] \\
&= \int_{\mathbf{r}} v_{\text{ext}}\, n_0\, d\mathbf{r} + \sum_i^N \epsilon_i - \int_{\mathbf{r}} v_s[n_0]\, n_0\, d\mathbf{r} + E_H[n_0] + E_{xc}[n_0] \\
&= \int_{\mathbf{r}} (v_{\text{ext}} - v_s)\; n_0\, d\mathbf{r} + \sum_i^N \epsilon_i + E_H[n_0] + E_{xc}[n_0] \\
&= \int_{\mathbf{r}} \left[v_{\text{ext}} - \left(v_{\text{ext}} + \int_{\mathbf{r}} \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' + v_{xc} \right) \right] n_0\, d\mathbf{r} + \sum_i^N \epsilon_i + E_H[n_0] + E_{xc}[n_0], \\
&= -\int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n_0(\mathbf{r}') n_0(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'\, d\mathbf{r} - \int_{\mathbf{r}} v_{xc}\, n_0\, d\mathbf{r} + \sum_i^N \epsilon_i + E_H[n_0] + E_{xc}[n_0] \\
&= -2E_H[n_0] - \int_{\mathbf{r}} v_{xc}\, n_0\, d\mathbf{r} + \sum_i^N \epsilon_i + E_H[n_0] + E_{xc}[n_0]
\end{aligned}
$$

$$
\boxed{E_0 = -\int_{\mathbf{r}} v_{xc}\, n_0\, d\mathbf{r} + \sum_i^N \epsilon_i - E_H[n_0] + E_{xc}[n_0]}
$$

Resolution of the Kohn-Sham equations

Diagonalisation

1 Take n^{old} as input for self-consistency equation,

$$v_s(\mathbf{r})^{old} = v_{\text{ext}}(\mathbf{r}) + \int_{\mathbf{r}} d\mathbf{r}' \frac{n(\mathbf{r}')^{old}}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}(\mathbf{r}, [n^{old}])$$

2 Solve (by diagonalisation) Schrödinger equation for NI electrons $\rightarrow \{\phi^{new}\}$

$$\left(-\frac{1}{2}\nabla^2 + v_s^{old}\right)\phi_i^{new} = \epsilon_i^{new}\phi_i^{new}$$

3 $n^{old} = \sum |\phi_i^{new}|^2$ and `goto 1` unless converged

Kohn-Sham scheme

Observations

- The Kohn-Sham equations must be solved *self-consistently*:

$$n(\mathbf{r}) \;\Rightarrow\; v_s[n] \;\Rightarrow\; \{\phi_i\} \;\Rightarrow\; n(\mathbf{r}) \;\Rightarrow\; \ldots$$

- The Kohn-Sham potential is *local*

- The eigenvalues are *not* physical, except for the one of the highest occupied orbital, which is (should be) the ionisation potential

- The eigenvectors ϕ_i are *not* any single-particle orbitals

- Please remember: DFT is a *ground state theory*

- The exact functional is not known (at the time being)