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Density-Functional Perturbation Theory : basics

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Plan

1. Material properties from total energy derivatives
2. The treatment of perturbations in ordinary quantum mechanics
3. Perturbation theory of variational principles
4. Density-Functional Perturbation Theory

References :

S. Baroni, P. Giannozzi and A. Testa, *Phys. Rev. Lett.* 58, 1861 (1987)
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S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozzi, *Rev. Mod. Phys.* 73, 515 (2001)

Density Functional Theory

* Total energy and density as a function of Kohn-Sham wavefunctions

$$E_{el} = \quad {}_{,occ} \langle \quad |T+\underline{\underline{V}}| \quad \rangle + E_{Hxc}[\quad]$$

$$(\vec{r}) = \quad {}_{,occ} \quad (\vec{r}) \quad (\vec{r})$$

Either : solve Kohn-Sham equations self-consistently

or : minimize E_{el} (variational !) under orthonormalization constraints.

Can use different representations of wavefunctions

Fix the potential => fix the system
(unit cell parameters, nuclei types and positions)

Here, compute the response of the system to small modifications...

Density - Functional Perturbation Theory

Many physical properties are derivatives of the total energy
(or a suitable thermodynamic potential) with respect to perturbations.

Let us consider the following perturbations :

- atomic displacements (phonons)
- dilatation/contraction of the primitive cell
- homogeneous external field (electric field ...)

Derivatives of the total energy (electronic part + nuclei-nuclei interaction) :

1st order derivatives : forces, stresses, dipole moment ...

2nd order derivatives : dynamical matrix, elastic constants, dielectric susceptibility
atomic polar tensors or Born effective charge tensors
piezoelectricity, internal strains

3rd order derivatives : non-linear dielectric susceptibility
phonon - phonon interaction, Grüneisen parameters, ...

Further properties obtained by integration over phononic degrees of freedom :
entropy, thermal expansion, phonon-limited thermal conductivity ...

Perturbations

* Variation of energy and density around a fixed potential

$$E_{el}(\quad) = \Big)_{,occ} \langle \quad (\quad) | \hat{T} + \underline{\underline{\hat{V}}}(\quad) | \quad (\quad) \rangle + E_{Hxc} \quad (\quad) (\quad$$

$$(\vec{r};\quad) = \Big)_{,occ} \quad ^{*}(\vec{r};\quad) \quad (\vec{r};\quad)$$

* Perturbations (assumed known through all orders)

$$\hat{V}(\quad) = \hat{V}^{(0)} + \quad \hat{V}^{(1)} + \quad ^{2}\hat{V}^{(2)} + \ldots$$

i.e. : to investigate phonons, the parameter of the perturbation governs linearly the nuclei displacement, but note that the change of potential is non-linear in this parameter.

$$V_{ph}(\vec{r}) = \sum_{:\,nuclei} V\,(\vec{r} - (\vec{a} + \vec{u}\ )) - V\,(\vec{r} - \vec{a}\ )$$

$$\vec{u} \quad = \quad \vec{e} \quad cos(\vec{q} \, . \, \vec{a}\ )$$

small parameter

'polarisation' of the phonon

phonon wavevector

More perturbations ...

* Dilatation / Contraction

$$r' = r$$

$$= + .$$

small parameter

* $\frac{}{\vec{q}}$ of another perturbation

* 'Alchemical' perturbation

$. \hat{V}_{A \quad B}$ [for example $V_{Pb \quad Au} = V_{Au} - V_{Pb}$]

$. \hat{V}_{so}$

* $\frac{}{t}$ in classical dynamics for ions

* $\vec{B}$ Magnetic field

Total energy changes

$$E = E^{(0)} + \; E^{(1)} + \; {}^{2}E^{(2)} + \ldots$$

2nd order derivatives : dielectric susceptibility
elastic constants
dynamical matrix

=Linear - response theory : Baroni, Giannozzi, Testa, Phys. Rev. Lett. 58, 1861 (1987)

3rd order derivatives : non-linear responses

X. Gonze & J.-P. Vigneron, *Phys. Rev. B* 39, 13120 (1989)

DFPT allows to compute $E^{(1)}$, $E^{(2)}$ (as well as $E^{(3)}$, $E^{(4)}$ ...)

X.Gonze *Phys. Rev A* 52, 1096 (1995)

$$= \; {}^{(0)} + \; {}^{(1)} + {}^{2} \; {}^{(2)} + \ldots$$

How is it possible to get energy derivatives ?

* Finite Differences

Compare $E\left\{\ ;\ V_{ext}\right\}$ and $E'\left\{\ ';\ V'_{ext}\right\}$

'Direct' Approach (Frozen phonons ...)
[Note problem with commensurability]

* Hellman - Feynman theorem (for $E^{(1)}$)

Due to variational character : $\frac{E}{} = 0$

$$\frac{dE}{d} = \frac{E}{V_{ext}}\frac{V_{ext}}{} + \underset{\overset{||}{0}}{\frac{E}{}} \cdot \underset{\overset{\downarrow}{(1)}}{\frac{}{}} = \frac{E}{V_{ext}}V_{ext}^{(1)}$$

In order to get $E^{(1)}$ we do not need ${}^{(1)}$

General framework of perturbation Theory

* $A(\quad) = A^{(0)} + \quad A^{(1)} + \quad {}^{2}A^{(2)} + \quad {}^{3}A^{(3)} \ldots$

* $E\{\quad ; V_{ext}\}$

Hypothesis : we know $V_{ext}(\quad) = V_{ext}^{(0)} + \quad V_{ext}^{(1)} + \quad {}^{2}V_{ext}^{(2)} + \ldots$

through all orders, as well as $\quad {}^{(0)}, n^{(0)}, E^{(0)}$

We would like to calculate

$E^{(1)}, E^{(2)}, E^{(3)} \ldots$

$n^{(1)}, n^{(2)}, n^{(3)} \ldots$

${}^{(1)}, \quad {}^{(2)}, \quad {}^{(3)} \ldots$

${}^{(1)}, \quad {}^{(2)}, \quad {}^{(3)} \ldots$

Perturbation theory for ordinary quantum mechanics

$$(\hat{H} - \quad)\,|\quad\rangle = 0$$ (Schrödinger equation)

$$\langle\quad|\quad\rangle = 1$$ (normalisation condition)

$$\langle\quad|\hat{H} - \quad|\quad\rangle = 0$$

or $$\quad = \langle\quad|\hat{H}|\quad\rangle$$ (expectation value)

The Hamiltonian is supposed known through all orders

$$\hat{H} = \hat{H}^{(0)} + \quad \hat{H}^{(1)} + \quad {}^{2}\hat{H}^{(2)} + \ldots = \quad_{n} \quad {}^{n}\hat{H}^{(n)}$$

Perturbation expansion of the Schrödinger Equation

Suppose $\hat{H}(\ )\,|\ {}_n(\ )\rangle = {}_n\,|\ {}_n(\ )\rangle$ valid for all

with
$$\begin{cases} \hat{H}(\ ) = \hat{H}^{(0)} + \ \hat{H}^{(1)} \\ {}_n(\ ) = {}^{(0)}_n + \ {}^{(1)}_n + {}^2\ {}^{(2)}_n + \ldots \\ {}_n(\ ) = {}^{(0)}_n + \ {}^{(1)}_n + {}^2\ {}^{(2)}_n + \ldots \end{cases}$$

One expands the Schrödinger equation:

$$\hat{H}^{(0)}|\ {}^{(0)}_n\rangle + \ \left(\hat{H}^{(1)}|\ {}^{(0)}_n\rangle + \hat{H}^{(0)}|\ {}^{(1)}_n\rangle\right) + {}^2\left(\hat{H}^{(1)}|\ {}^{(1)}_n\rangle + \hat{H}^{(0)}|\ {}^{(2)}_n\rangle\right) + \ldots$$
$$= {}^{(0)}_n|\ {}^{(0)}_n\rangle + \ \left({}^{(1)}_n|\ {}^{(0)}_n\rangle + {}^{(0)}_n|\ {}^{(1)}_n\rangle\right) + {}^2\left({}^{(2)}_n|\ {}^{(0)}_n\rangle + {}^{(1)}_n|\ {}^{(1)}_n\rangle + {}^{(0)}_n|\ {}^{(2)}_n\rangle\right) + \ldots$$

In $\ = 0$, one gets $\hat{H}^{(0)}|\ {}^{(0)}_n\rangle = {}^{(0)}_n|\ {}^{(0)}_n\rangle$ no surprise …

Derivation with respect to , then $\ = 0$ (=first order of perturbation)

$$\Rightarrow \hat{H}^{(1)}|\ {}^{(0)}_n\rangle + \hat{H}^{(0)}|\ {}^{(1)}_n\rangle = {}^{(1)}_n|\ {}^{(0)}_n\rangle + {}^{(0)}_n|\ {}^{(1)}_n\rangle$$

2 derivations with respect to , then $\ = 0$ (=second order of perturbation)

$$\Rightarrow \hat{H}^{(1)}|\ {}^{(1)}_n\rangle + \hat{H}^{(0)}|\ {}^{(2)}_n\rangle = {}^{(2)}_n|\ {}^{(0)}_n\rangle + {}^{(1)}_n|\ {}^{(1)}_n\rangle + {}^{(0)}_n|\ {}^{(2)}_n\rangle$$

Perturbation expansion of the normalisation condition

If $\quad \forall : \langle \;_n(\forall) | \;_n(\forall) \rangle = 1$

with $\quad {}_n(\;) = {}^{(0)}_n + {}^{(1)}_n + {}^{2}\,{}^{(2)}_n + \ldots$

With the same technique than for the Schrödinger equation, one deduces

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

no surprise …

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

$$\langle {}^{(2)}_n | {}^{(0)}_n \rangle + \langle {}^{(1)}_n | {}^{(1)}_n \rangle + \langle {}^{(0)}_n | {}^{(2)}_n \rangle = 0$$

Hellmann & Feynman theorem : ${}^{(1)}_{n}$

Starting from the first-order Schrödinger equation

$$\hat{H}^{(1)} \left| {}^{(0)}_{n} \right\rangle + \hat{H}^{(0)} \left| {}^{(1)}_{n} \right\rangle = {}^{(1)}_{n} \left| {}^{(0)}_{n} \right\rangle + {}^{(0)}_{n} \left| {}^{(1)}_{n} \right\rangle$$

Premultiplication by $\left\langle {}^{(0)}_{n} \right|$

$$\left\langle {}^{(0)}_{n} \right| \hat{H}^{(1)} \left| {}^{(0)}_{n} \right\rangle + \underbrace{\underbrace{\left\langle {}^{(0)}_{n} \right| \hat{H}^{(0)}}_{\left\langle {}^{(0)}_{n} \right| {}^{(0)}_{n}} \left| {}^{(1)}_{n} \right\rangle} = {}^{(1)}_{n} \underbrace{\left\langle {}^{(0)}_{n} \middle| {}^{(0)}_{n} \right\rangle}_{=1} + \underbrace{{}^{(0)}_{n} \left\langle {}^{(0)}_{n} \middle| {}^{(1)}_{n} \right\rangle}$$

So : $\boxed{{}^{(1)}_{n} = \left\langle {}^{(0)}_{n} \right| \hat{H}^{(1)} \left| {}^{(0)}_{n} \right\rangle}$ = Hellmann & Feynman theorem

Notes :

* ${}^{(0)}_{n}$ and $\hat{H}^{(1)}$ are supposed known
* ${}^{(1)}_{n}$ is not needed
* ${}^{(1)}_{n} = \left.\frac{d\ {}_{n}}{d}\right|_{=0}$
* $\left\langle {}^{(0)}_{n} \right| \hat{H}^{(1)} \left| {}^{(0)}_{n} \right\rangle$ = expectation value of the Hamiltonian for the non-perturbed wavefunction
* generalisation

$$\left.\frac{d\ {}_{n}}{d}\right| = \left\langle {}_{n}(\ ) \right| \frac{d\hat{H}}{d} \left| {}_{n}(\ ) \right\rangle$$

${}^{(1)}_{n}$ OK !

The second order derivative of total energy $\;^{(2)}_{n}$

Starting from the second-order Schrödinger equation

$$\hat{\mathrm{H}}^{(1)}\left|\;^{(1)}_{\mathrm{n}}\right\rangle + \hat{\mathrm{H}}^{(0)}\left|\;^{(2)}_{\mathrm{n}}\right\rangle = \;^{(2)}_{\mathrm{n}}\left|\;^{(0)}_{\mathrm{n}}\right\rangle + \;^{(1)}_{\mathrm{n}}\left|\;^{(1)}_{\mathrm{n}}\right\rangle + \;^{(0)}_{\mathrm{n}}\left|\;^{(2)}_{\mathrm{n}}\right\rangle$$

Premultiplication by $\left\langle\;^{(0)}_{\mathrm{n}}\right|$

$$\begin{aligned} ^{(2)} &= \left\langle\;^{(0)}\middle|\hat{H}^{(1)} - \;^{(1)}\middle|\;^{(1)}\right\rangle \\ &= \frac{1}{2}\left(\left\langle\;^{(0)}\middle|\hat{H}^{(1)}\middle|\;^{(1)}\right\rangle + \left\langle\;^{(1)}\middle|\hat{H}^{(1)}\middle|\;^{(0)}\right\rangle\right) \end{aligned}$$

No knowledge of $\;^{(2)}$ is needed, but one needs $\;^{(1)}$! How to get it ?

In search of $^{(1)}_{n}$

Again the first-order Schrödinger equation :

$$\underline{\hat{H}^{(1)}}\,\Big|\,\underline{\ }^{(0)}_{n}\Big\rangle + \underline{\hat{H}^{(0)}}\Big|\,{}^{(1)}_{n}\Big\rangle = \underline{{}^{(1)}_{n}}\Big|\,\underline{\ }^{(0)}_{n}\Big\rangle + \underline{{}^{(0)}_{n}}\Big|\,{}^{(1)}_{n}\Big\rangle$$

known known

Terms containing $\Big|\,{}^{(1)}_{n}\Big\rangle$ are gathered :

$$\left(\underline{\hat{H}^{(0)} - {}^{(0)}_{n}}\right)\Big|\,{}^{(1)}_{n}\Big\rangle = -\left(\underline{\hat{H}^{(1)} - {}^{(1)}_{n}\Big)\Big|\,{}^{(0)}_{n}}\Big\rangle$$

(called Sternheimer equation)

Equivalence with the matrix equation (systeme of linear equations)

$$\underline{\underline{A}} \cdot \underline{x} = \underline{y}$$

usually solved by $\underline{x} = \underline{\underline{A}}^{-1}\,\underline{y}$ if $\underline{\underline{A}}^{-1}$ exist.

Problem : $\left(\hat{H}^{(0)} - {}^{(0)}_{n}\right)$ is not invertible !

Indeed $\left(\hat{H}^{(0)} - {}^{(0)}_{n}\right)\Big|\,{}^{(0)}_{n}\Big\rangle = \hat{H}^{(0)}\Big|\,{}^{(0)}_{n}\Big\rangle - {}^{(0)}_{n}\Big|\,{}^{(0)}_{n}\Big\rangle = |0\rangle$

Sum-over-states solution of the Sternheimer equation

$$\hat{H}^{(0)} - {}^{(0)}_{n} \,\Big|\, {}^{(1)}_{n} \Big\rangle = - \left(\hat{H}^{(1)} - {}^{(1)}_{n} \right) \Big|\, {}^{(0)}_{n} \Big\rangle$$

Define the complete orthonormal basis associated to $\hat{H}^{(0)}$

$$\left\{ {}^{(0)}_{m} \right\} \text{ such that } \hat{H}^{(0)} \Big|\, {}^{(0)}_{m} \Big\rangle = {}^{(0)}_{m} \,\Big|\, {}^{(0)}_{m} \Big\rangle$$

Représentation of the Sternheimer equation in this basis

$$C^{(1)}_{mn} = \Big\langle\, {}^{(0)}_{m} \Big|\, {}^{(1)}_{n} \Big\rangle \qquad \Big|\, {}^{(1)}_{n} \Big\rangle = {}_{m} \, C^{(1)}_{mn} \,\Big|\, {}^{(0)}_{m} \Big\rangle$$

$$m \quad \Big\langle \forall^{(0)}_{m} \Big| \hat{H}^{(0)} - {}^{(0)}_{n} \Big| \forall^{(1)}_{n} \Big\rangle = - \Big\langle \forall^{(0)}_{m} \Big| \hat{H}^{(1)} - {}^{(1)}_{n} \Big| \forall^{(0)}_{n} \Big\rangle$$

$$\left({}^{(0)}_{m} - {}^{(0)}_{n} \right) \Big\langle \forall^{(0)}_{m} \Big| \forall^{(1)}_{n} \Big\rangle = - \Big\langle \forall^{(0)}_{m} \Big| \hat{H}^{(1)} \Big| \forall^{(0)}_{n} \Big\rangle + {}^{(1)}_{n} \Big\langle \forall^{(0)}_{m} \Big| \forall^{(0)}_{n} \Big\rangle$$

$$\left({}^{(0)}_{m} - {}^{(0)}_{n} \right) C^{(1)}_{mn} = - \Big\langle \forall^{(0)}_{m} \Big| \hat{H}^{(1)} \Big| \forall^{(0)}_{n} \Big\rangle + {}^{(1)}_{n} \quad {}_{mn}$$

Sum-over-states solution of the Sternheimer equation (II)

$$\left({}^{(0)}_{m} - {}^{(0)}_{n} \right) C^{(1)}_{mn} = - \left\langle {}^{(0)}_{m} \middle| \hat{H}^{(1)} \middle| {}^{(0)}_{n} \right\rangle + {}^{(1)}_{n} \;\; {}_{mn}$$

(1) For m = n, $\quad 0 \, . \, C^{(1)}_{nn} = - \left\langle {}^{(0)}_{n} \middle| H^{(1)} \middle| {}^{(0)}_{n} \right\rangle + {}^{(1)}_{n}$

$= 0$ due to Hellmann & Feynman theorem

=> $C^{(1)}_{nn}$ undetermination

(2) For m ≠ n, $\quad \underset{\equiv}{\text{si}} \;\; {}^{(0)}_{m} - {}^{(0)}_{n} \quad 0$ (non degenerate case)

$$C^{(1)}_{mn} = - \frac{\left\langle {}^{(0)}_{m} \middle| \hat{H}^{(1)} \middle| {}^{(0)}_{n} \right\rangle}{{}^{(0)}_{m} - {}^{(0)}_{n}}$$

Thus $$\left| {}^{(1)}_{n} \right\rangle = C^{(1)}_{nn} \left| {}^{(0)}_{n} \right\rangle - \sum_{m(\;\;n)} \frac{\left| {}^{(0)}_{m} \right\rangle \left\langle {}^{(0)}_{m} \middle| \hat{H}^{(1)} \middle| {}^{(0)}_{n} \right\rangle}{{}^{(0)}_{m} - {}^{(0)}_{n}}$$

actually, the undetermined coefficient can be set to 0 !

The 1st order derivative of the wavefunctions

(1) $(\hat{H}^{(0)} - \ ^{(0)})\left|\ ^{(1)}\right\rangle = -(\hat{H}^{(1)} - \ ^{(1)})\left|\ ^{(0)}\right\rangle$

(Sternheimer equation)

Should be inverted to find $\left|\ ^{(1)}\right\rangle$

Operator $(\hat{H}^{(0)} - \ ^{(0)})^{-1}$ is singular

projection on subspace to $\left|\ ^{(0)}\right\rangle$

(2) $P \ (\hat{H}^{(0)} - \ ^{(0)})P \ \left|\ ^{(1)}\right\rangle = -P \ \hat{H}^{(1)}\left|\ ^{(0)}\right\rangle$

(3) $\hat{P}\ \left|\ ^{(1)}\right\rangle = \hat{G}\ (E\ )\,\hat{H}^{(1)}\left|\ ^{(0)}\right\rangle$

where $\hat{G}\ (E\ ) = \hat{P}\ [\hat{P}\ (\ ^{(0)} - \hat{H}^{(0)})\hat{P}\ ]^{-1}\ \hat{P}$

(Green's function technique)

(4) $\hat{P}\ \left|\ ^{(1)}\right\rangle = \ \left|\ ^{(0)}\right\rangle \frac{1}{-} \left\langle\ ^{(0)}\right|\hat{H}^{(1)}\left|\ ^{(0)}\right\rangle$

(Sum Over States technique)

The computation of $^{(3)}$ (I)

* Starting from (now we consider higher-order contributions for the Hamiltonian again)

$$(\hat{H}^{(0)} - \ ^{(0)})\left|\ ^{(3)}\right\rangle + (\hat{H}^{(1)} - \ ^{(1)})\left|\ ^{(2)}\right\rangle + (\hat{H}^{(2)} - \ ^{(2)})\left|\ ^{(1)}\right\rangle + (\hat{H}^{(3)} - \ ^{(3)})\left|\ ^{(0)}\right\rangle = 0$$

Premultiply by $\left\langle\ ^{(0)}\right|$ gives

$$\begin{aligned} ^{(3)} = & \left\langle\ ^{(0)}\right|\hat{H}^{(3)}\left|\ ^{(0)}\right\rangle \\ & + \left\langle\ ^{(0)}\right|\hat{H}^{(2)} - \ ^{(2)}\left|\ ^{(1)}\right\rangle \\ & + \left\langle\ ^{(0)}\right|\hat{H}^{(1)} - \ ^{(1)}\left|\ ^{(2)}\right\rangle \end{aligned}$$

⚠ $^{(2)}$ is needed in this formula

The computation of $^{(3)}$ (II)

* However, the perturbation expansion of $0 = \langle \quad | \hat{H} - \quad | \quad \rangle$ at third order gives:

$$
\begin{aligned}
0 = \; & \langle \,^{(0)} | \hat{H}^{(3)} - \,^{(3)} | \,^{(0)} \rangle + \langle \,^{(1)} | \hat{H}^{(2)} - \,^{(2)} | \,^{(0)} \rangle + \langle \,^{(2)} | \hat{H}^{(1)} - \,^{(1)} | \,^{(0)} \rangle + \langle \,^{(3)} | \hat{H}^{(0)} - \,^{(0)} | \,^{(0)} \rangle \\
& + \langle \,^{(0)} | \hat{H}^{(2)} - \,^{(2)} | \,^{(1)} \rangle + \langle \,^{(1)} | \hat{H}^{(1)} - \,^{(1)} | \,^{(1)} \rangle + \langle \,^{(2)} | \hat{H}^{(0)} - \,^{(0)} | \,^{(1)} \rangle \\
& + \langle \,^{(0)} | \hat{H}^{(1)} - \,^{(1)} | \,^{(2)} \rangle + \langle \,^{(1)} | \hat{H}^{(0)} - \,^{(0)} | \,^{(2)} \rangle \\
& + \langle \,^{(0)} | \hat{H}^{(0)} - \,^{(0)} | \,^{(3)} \rangle
\end{aligned}
$$

It can be seen that the sum of terms in a row or in a column vanishes ! (Exercice !)
We get rid off the two last columns and the two last rows, rearrange the equation, and get:

$$
\begin{aligned}
^{(3)} = \; & \langle \,^{(0)} | \hat{H}^{(3)} | \,^{(0)} \rangle + \langle \,^{(1)} | \hat{H}^{(2)} | \,^{(0)} \rangle \\
& + \langle \,^{(0)} | \hat{H}^{(2)} | \,^{(1)} \rangle + \langle \,^{(1)} | \hat{H}^{(1)} - \,^{(1)} | \,^{(1)} \rangle
\end{aligned}
$$

[We have used $\langle \,^{(0)} | \,^{(0)} \rangle = 1$ and $\langle \,^{(0)} | \,^{(1)} \rangle + \langle \,^{(1)} | \,^{(0)} \rangle = 0$]

⚠ $^{(2)}$ is not needed in this formula

Variational Principle for the lowest ${}_{n}^{(2)}$ (Hylleraas principle)

$$^{(2)} = \min_{(1)} \left\{ \left\langle {}^{(1)} \middle| \hat{H}^{(1)} \middle| {}^{(0)} \right\rangle + \left\langle {}^{(1)} \middle| \hat{H}^{(0)} - {}^{(0)} \middle| {}^{(1)} \right\rangle + \left\langle {}^{(0)} \middle| \hat{H}^{(2)} \middle| {}^{(0)} \right\rangle + \left\langle {}^{(0)} \middle| \hat{H}^{(1)} \middle| {}^{(1)} \right\rangle \right\}$$

with the following constraint on ${}^{(1)}$:

$$\left\langle {}^{(0)} \middle| {}^{(1)} \right\rangle + \left\langle {}^{(1)} \middle| {}^{(0)} \right\rangle = 0$$

It allows to recover Sternheimer's equation :

$\frac{}{{}^{(1)}}$ [...] = 0 + a Lagrange multiplier

$$(\hat{H}^{(0)} - {}^{(0)}) \left| {}^{(1)} \right\rangle + (\hat{H}^{(1)} - {}^{(1)}) \left| {}^{(0)} \right\rangle = 0$$

Equivalence of :
* Minimization of ${}^{(2)}$
* Sternheimer equation
* Green's function technique
* Sum over States
* Finite differences + limit

Perturbation of a variational principle (I)

$E^{(0)}\left\{ \;^{(0)} \right\}$ variational

$E^{(1)}\left\{ \;^{(0)} \right\}$ (Hellman -Feynman) non-variational

$E^{(2)}\left\{ \;^{(0)};\;^{(1)} \right\}$ "

$E^{(3)}\left\{ \;^{(0)};\;^{(1)};\;^{(2)} \right\}$ "

$\vdots$

Is it the best ?

* Let us suppose that we know the correct wavefunctions $-$ through order $^{n-1}$

$$- = \;_{n-1} + O(\;^{n}) \quad \text{where} \quad _{n-1} = \;^{(0)} + \;^{(1)} + \ldots + \;^{n-1}\;^{(n-1)}$$

* Variational property of the energy functional

$$E\left\{ \;_{trial} + \mathrm{O}(\;) \right\} = E\left\{ \;_{trial} \right\} + \mathrm{O}(\;^{2})$$

* Set $\;_{trial} = \;_{n-1}\;; \quad = \;^{n}$

$$E\left\{ \;_{n-1} \right\} = E\left\{ \; \right\} + O(\;^{2n})$$

the knowledge of $\;_{n-1}$ gives E up to order $\;^{2n-1}$

the knowledge of $\;_{n}$ gives E up to order $\;^{2n+1}$

'$2n+1$ theorem'

Perturbation of a variational principle (II)

* If the variational principle is an external principle

[the error is either > 0 - minimal principle -

or < 0 - maximal principle -]

the leading missing term is also of definite signe also an extremal principle

To summarize :

$E^{(0)} \left\{ {}^{(0)} \right\}$ variational

$E^{(1)} \left\{ {}^{(0)} \right\}$

$E^{(2)} \left\{ {}^{(0)}; \; {}^{(1)} \right\}$ variational with respect to ${}^{(1)}$

$E^{(3)} \left\{ {}^{(0)}; \; {}^{(1)} \right\}$

$E^{(4)} \left\{ {}^{(0)}; \; {}^{(1)}; \; {}^{(2)} \right\}$ variational with respect to ${}^{(2)}$

$E^{(5)} \left\{ {}^{(0)}; \; {}^{(1)}; \; {}^{(2)} \right\}$

Note : for mixed derivatives, similar expressions exists; however the extremal property is lost, but the 'stationarity' is preserved

$$\left.\begin{array}{l} E^{j_1 j_2} \left\{ {}^{(0)}; \; {}^{j_1} \right\} \\ E^{j_1 j_2} \left\{ {}^{(0)}; \; {}^{j_2} \right\} \end{array}\right\} \text{exist ! but non-stationary}$$

$E^{j_1 j_2} \left\{ {}^{(0)}; \; {}^{j_1}; \; {}^{j_2} \right\}$ stationary

Basic equations in DFT

DFT

Minimize $E_{el}\{\quad\} = {}^{occ}\langle \quad |\hat{T}+\hat{V}| \quad \rangle + E_{Hxc}[\quad]$

with $\quad (\vec{r}) = {}^{occ} \quad {}^{*}(\vec{r}) \quad (\vec{r})$

under constraint $\langle \quad | \quad \rangle =$

or solve self-consistently Kohn-Sham equations, with

$$\hat{H}| \quad \rangle = \quad | \quad \rangle$$

$$\hat{H} = \hat{T}+\hat{V}+\frac{E_{Hxc}}{\quad}$$

Basic equations in DFPT

DFPT

Minimize wrt $^{(1)}$:

$$E_{el}^{(2)}\left\{ {}^{(1)}; {}^{(0)} \right\} = {}^{occ} \left\langle {}^{(1)} \middle| \hat{H}^{(0)} - {}^{(0)} \middle| {}^{(1)} \right\rangle + \left\langle {}^{(1)} \middle| \hat{V}^{(1)} \middle| {}^{(0)} \right\rangle$$

$$+ \left\langle {}^{(0)} \middle| \hat{V}^{(1)} \middle| {}^{(1)} \right\rangle + \left\langle {}^{(0)} \middle| \hat{V}^{(2)} \middle| {}^{(0)} \right\rangle$$

$$+ \frac{1}{2} \frac{{}^{2}E_{Hxc}}{(\vec{r}) \quad (\vec{r}')} {}^{(1)}(\vec{r}) \; {}^{(1)}(\vec{r}')\, d\vec{r}\, d\vec{r}'$$

with $${}^{(1)}(\vec{r}) = {}^{occ} \; {}^{(1)*}(\vec{r}) \; {}^{(0)}(\vec{r}) + {}^{(0)*}(\vec{r}) \; {}^{(1)}(\vec{r})$$

under constraint $$\left\langle {}^{(0)} \middle| {}^{(1)} \right\rangle = 0$$

or solve self-consistently the Sternheimer equation, with

$$(\hat{H}^{(0)} - {}^{(0)}) \left| {}^{(1)} \right\rangle = - (\hat{H}^{(1)} - {}^{(1)}) \left| {}^{(0)} \right\rangle$$

$$\hat{H}^{(1)} = \hat{V}^{(1)} + \frac{{}^{2}E_{Hxc}}{(r) \quad (r')} {}^{(1)}(r')dr'$$

$${}^{(1)} = \left\langle {}^{(0)} \middle| \hat{H}^{(1)} \middle| {}^{(0)} \right\rangle$$

Order of calculations in DFPT (for linear-response)

(1) Ground-state calculation

$$V_{ext}^{(0)} \qquad {}^{(0)}, n^{(0)}$$

(2) Do for each perturbation j_1

- use ${}^{(0)}, n^{(0)}$
- $V_{ext}^{j1} \qquad {}^{j1}, n^{j1}$ using minimization of second-order energy
  or
  Sternheimer equation

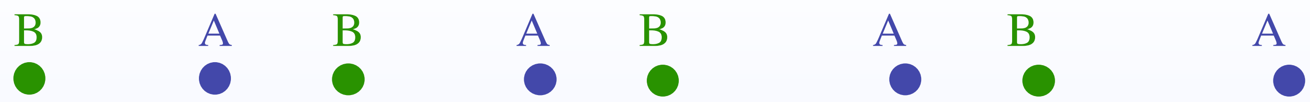
Enddo

(3) Do for each $\{ j_{1,} j_2 \}$

either get $E^{j1\,j2}$ stationary using both ^{j1} and ^{j2}
or get $E^{j1\,j2}$ using ^{j1}
Enddo

(4) Post-processing : from 'bare' $E^{j1\,j2}$ to physical properties

Example : 1-dimensional diatomic linear chain [only phonons]



ph$_A$

ph$_B$

E

$\vec{E} . \vec{r}$

.

(coordinate dilatation)

(2) Get ph_A, ph_B, E, for all bands, self-consistently

(3) Get $E^{j1\,j2}$

	ph_A	ph_A	E	
ph_A	D^{anal}_{AA}	D^{anal}_{AB}	Z_A	$_A$
ph_B	D^{anal}_{AB}	D^{anal}_{BB}	Z_B	$_B$
E	Z_A	Z_B		$\bar{\text{f}}$
	$_A$	$_B$	$\bar{\text{f}}$	$\bar{\text{c}}$

either stationary or interchange

$E = 0$ fixed or $D = 0$ fixed

(4) Get physical properties [schematic formulas ...]

$$D = D^{anal} + \frac{Z^* Z^*}{}$$

$$(\quad) = \quad + \frac{Z^* Z^*}{D - M \quad ^2}$$

$$c = \bar{c} + \frac{}{D^{anal}}$$

Treatment of phonons : factorization of the phase

* Suppose the unperturbed system is periodic

$$V^{(0)}(\vec{r}+\vec{R}_a) = V^{(0)}(\vec{r})$$

* If the perturbation is characterized by a wavevector :

$$V^{(1)}(\vec{r}+\vec{R}_a) = e^{i\vec{q}.\vec{R}_a} \; V^{(1)}(\vec{r})$$

all the responses, at linear order, will also be characterized by a wavevector :

$$n^{(1)}(\vec{r}+\vec{R}_a) = e^{i\vec{q}.\vec{R}_a} \; n^{(1)}(\vec{r})$$

$${}^{(1)}_{m,\vec{k},\vec{q}}(\vec{r}+\vec{R}_a) = e^{i(\vec{k}+\vec{q})\vec{R}_a} \quad {}^{(1)}_{m,\vec{k},\vec{q}}(\vec{r})$$

...

* Now, we define related periodic quantities

$$\bar{n}^{(1)}(\vec{r}) = e^{-i\vec{q}\,\vec{r}} \; n^{(1)}(\vec{r})$$

$$u^{(1)}_{m,\vec{k},\vec{q}}(\vec{r}) = (N \quad {}_0)^{1/2} \; e^{-i(\vec{k}+\vec{q})\vec{r}} \quad {}^{(1)}_{m,\vec{k},\vec{q}}(\vec{r})$$

* In the equations of DFPT, only these periodic quantities appear: the phases

$e^{-i\vec{q}.\vec{r}}$ and $e^{-i(\vec{k}+\vec{q})\vec{r}}$ can be factorized

* The treatment of perturbations incommensurate with the unperturbed system periodicity, including electric fields, is mapped onto the original periodic system.