DENSITY MATRIX DENSITY FUNCTIONAL PERTURBATION THEORY

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OUTLINE

- General definition of perturbation theory
- Density functional perturbation theory
- Density matrix density functional perturbation theory

GENERAL DEFINITION OF PERTURBATION THEORY

In general all quantities (operators, wavefunctions, observables) depend on parameter(s) λ (e.g. atomic cooordinates, components of uniform external electric field, cell dimensions of periodic systems etc.)

It is assumed that each generic quantity $X(\lambda)$ of the system can be written as a perturbation series (Taylor series):

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \cdots$$

where

$$X^{(n)} = \frac{1}{n!} \frac{\partial^n X}{\partial \lambda^n}\bigg|_{\lambda=0}$$

In the case of a functional which obeys a variational principle, (such as the energy in density functional theory)

$$E[\Phi_{min}(\lambda); \lambda] = \min_{\Phi_{trial}(\lambda)} \{E[\Phi_{trial}(\lambda); \lambda]\}$$

there are two important theorems which apply:

2n+1 theorem: knowledge of up to $\Phi^{(n)}_{min}$ is sufficient for the determination of E up to $E^{(2n+1)}$.

This theorem allows us to calculate force constants (second order derivatives of energy w.r.t. atomic positions) and hence phonon spectra only from the first order corrections to the wavefunctions. It is also used to calculate third order derivatives (such as hyperpolarisabilities) but formulae become quite complicated with increasing order.

Even-order variational principle: For every even order of E there exists a variational principle of the form

$$E^{(2n)} = \min_{\Phi^{(n)}_{trial}} \left\{ \left(E \left[\sum_{i=0}^{n-1} \lambda^i \Phi^{(i)} + \lambda^n \Phi^{(n)}_{trial}; \lambda \right] \right)^{(2n)} \right\}$$

through which $\Phi^{(n)}$ and $E^{(2n)}$ can be determined.

A comprehensive analysis for the case of density functional theory can be found in:

X. Gonze. *Rhys. Rev. A* **52**(2) (1995) 1096.

DENSITY FUNCTIONAL PERTURBATION THEORY

Also known as "Linear response theory":

S. Baroni, S. de Gironcoli and A Dal Corso. *Rev. Mod. Phys.* **73**, (2001) 515.

In the quantum chemistry community it has been known as "Analytic second derivatives of the energy" or "Coupled-perturbed Hartree-Fock equations":

J. Gerratt and I. M. Mills. *J. Chem. Phys.* **49** 1719.

Start with Kohn-Sham equation (where H is the self-consistent Kohn-Sham Hamiltonian)

$$\hat{H}\psi_n = \epsilon_n \psi_n$$

Want to find out $\left.\frac{\partial \psi_n}{\partial \lambda}\right|_{\lambda=0} = \psi_n^{(1)}$

All unperturbed $\{\psi^{(0)}\}$ (valence and conduction functions together) are a complete set of functions, so expand solution in them

$$\psi_n^{(1)} = \sum_m |\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\psi^{(1)}\rangle = \sum_m \psi_m^{(0)} C_m$$

How to find C_m? Differentiate Kohn-Sham eigenvalue equation:

$$H^{(1)}\psi_n^{(0)} + H^{(0)}\psi_n^{(1)} = \epsilon_n^{(1)}\psi_n^{(0)} + \epsilon_n^{(0)}\psi_n^{(1)} \qquad (1)$$

Multiply by $\langle\psi_m^{(0)}|$ from the left to get

$$\psi_n^{(1)} = \sum_{m\neq n} \psi_m^{(0)} \frac{\langle\psi_m^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle}{\epsilon_n^{(0)} - \epsilon_m^{(0)}}$$

This equation involves sum over all states (conduction and valence) and it is not practical to use in most cases.

Instead of trying to expand $\psi_n^{(1)}$, in the set of all $\{\psi^{(0)}\}$ we can rearrange equation (1) to obtain the "Sternheimer" equation

$$(H^{(0)} - \epsilon_n^{(0)})\psi_n^{(1)} = -(H^{(1)} - \epsilon_n^{(1)})\psi_n^{(0)}$$

This is actually a linear system of equations that can be solved to get $\psi_n^{(1)}$. The righthand side depends on all $\psi_n^{(1)}$ that

belong to the set of (occupied) valence functions $\{\psi_v\}_{v=1}^{Nocc/2}$ because the derivative of the Kohn-Sham Hamiltonian is

$$H^{(1)} = V_{nuc}^{(1)}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \left. \frac{du_{xc}(n)}{dn} \right|_{n=n^{(0)}} n^{(1)}(\mathbf{r})$$

where

$$n^{(1)}(\mathbf{r}) = 4\mathrm{Re} \sum_{v=1}^{N_{occ}} \psi_v^{(0)*}(\mathbf{r}) \psi_v^{(1)}(\mathbf{r})$$

Hence we have a system of $N_{occ}/2$ linear nonhomogeneous equations each one of dimensions $M \times M$ where M is the size of the basis set.

These systems of equations are linearly coupled to each other so they need to be solved together either as a large $N_{occ}M/2 \times N_{occ}M/2$ system or by a self-consistent process for all smaller $M \times M$ systems.

Two major difficulties in solving the Sternheimer equation:

1. While the final results are invariant w.r.t. unitary rotations in the space of occupied orbitals, ("gauge invariant"), a choice of gauge has to be made which affects the solution process and the imosition of the orthonormality constraint.

2. In the case of periodic systems, the treatment of the perturbation due to a uniform electric field is problematic because the position operator $\mathbf{r}$ which describes this perturbation is not periodic.

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Derived (with formulae up to arbitray order) by:
M. Lazzeri and F. Mauri. *Phys. Rev. B* **68** (2003) 161101(R).

Rather than determining the Kohn-Sham orbitals, focus on the density matrix

$$\rho = \sum_{v=1}^{N_{occ}} |\psi_v\rangle\langle\psi_v|$$

Use projectors on valence and conduction zeroth order bands

$$P_V = \sum_v |\psi_v^{(0)}\rangle\langle\psi_v^{(0)}| = \rho^{(0)} \quad \text{and } P_C = \mathbf{1} - P_V$$

For a Hermitian operator A define

$$A_{CC} = P_C A P_C,\ A_{VV} = P_V A P_V, \text{ and}$$

$$A_{CV} = P_C A P_V, \text{ and } A_{VC} = (A_{CV})^\dagger$$

which leads to:

$$A = A_{CC} + A_{VV} + A_{CV} + A_{VC}$$

To find out $\rho^{(1)} = \rho^{(1)}_{CC} + \rho^{(1)}_{VV} + \rho^{(1)}_{CV} + \rho^{(1)}_{VC}$

1) From the idempotency property of the density matrix we have

$$\begin{aligned}
\rho &= \rho\rho \\
P_C\rho P_C &= P_C\rho(P_C + P_V)\rho P_C \\
\rho_{CC} &= \rho_{CC}\rho_{CC} + \rho_{CV}\rho_{VC} \\
\rho^{(1)}_{CC} &= \rho^{(1)}_{CC}\rho^{(0)}_{CC} + \rho^{(0)}_{CC}\rho^{(1)}_{CC} + \rho^{(1)}_{CV}\rho^{(0)}_{VC} + \rho^{(0)}_{CV}\rho^{(1)}_{VC} \\
\rho^{(1)}_{CC} &= \rho^{(1)}_{CC}\rho^{(0)}_{CC} + \rho^{(0)}_{CC}\rho^{(1)}_{CC} \\
\rho^{(1)}_{CC} &= \rho^{(1)}_{CC} + \rho^{(1)}_{CC} \\
\rho^{(1)}_{CC} &= 0
\end{aligned}$$

In a similar way we can show that $\rho^{(1)}_{VV} = 0$.

Therefore $\rho^{(1)} = \rho^{(1)}_{CV} + (\rho^{(1)}_{CV})^{\dagger}$ and we only need a way to find $\rho^{(1)}_{CV}$.

2) From the requirement that the density matrix commutes with the self-consistent (Kohn-Sham) Hamiltonian we have

$$\begin{aligned}
[H, \rho] &= 0 \\
[H^{(1)}, \rho^{(0)}] + [H^{(0)}, \rho^{(1)}] &= 0 \qquad (2)
\end{aligned}$$

also we can write $\rho^{(1)}_{CV}$ as

$$\rho^{(1)}_{CV} = \sum_{vc} |\psi^{(0)}_c\rangle\langle\psi^{(0)}_c|\rho^{(1)}|\psi^{(0)}_v\rangle\langle\psi^{(0)}_v| = \sum_{v} |\eta^{(1)}_v\rangle\langle\psi^{(0)}_v|$$

By multiplying the commutator sum of equation (2) by P_C from the left and $|\psi^{(0)}_v\rangle$ from the right we obtain

$$(H^{(0)} - \epsilon^{(0)}_v)|\eta^{(1)}_v\rangle = -P_C[H^{(1)}, \rho^{(0)}]|\psi^{(0)}_v\rangle$$

This system of coupled nonhomogeneous linear equations is identical in form to the Sternheimer equations and can be solved iteratively to determine the set of $\{\eta^{(1)}_v\}^{Nocc}_{v=1}$ and hence $\rho^{(1)}_{CV}$ and $\rho^{(1)}$.

The advantage of this approach is that the perturbed operator $[H^{(1)}, \rho^{(0)}]$ is well-defined in an extended insulator with periodic boundary conditions even if the perturbation λ is a uniform electric field. This is because the density matrix $\rho^{(0)}$ goes to zero exponentially and therefore $[\mathbf{r}, \rho^{(0)}]$ is localised in space (actually in the centres of the Wannier functions) rather than being extended. Also $\rho^{(1)}_{CV}$ is a gauge-invariant operator. This approach is also very suitable for calculating the first derivative of the polarisation.

$$\mathbf{P} = -\frac{2e}{N\Omega_c} Tr\{\mathbf{r}\rho^{(1)}\}$$

However, no-one has implemented this method yet to see how it works in practice!