DFPT: Density functional perturbation theory

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1 The formalism of DFT

1.1 Kohn, Sham and all that

We begin with the general many-body Schrodinger equation:

$$\widehat{\boldsymbol{H}}\Psi = \left(\sum_i^N \left(-\frac{\hbar^2}{2m_i}\nabla_i^2 \right) + \sum_i^N V(\vec{r_i}) + \sum_{i<j}^N U(\vec{r_i}, \vec{r_j}) \right) \Psi = E\Psi \tag{1}$$

For a single electron, one defines the probability density to be given by $n(\vec{r}) = \Psi^*(\vec{r})\Psi(\vec{r})$. In analogy, keeping in mind that electrons are indistinguishable, we can integrate over $N-1$ variables in the many-body function to arrive at the many body electron density:

$$n(\vec{r}) = N \int d\vec{r_2} \int d\vec{r_3} \ldots \int d\vec{r_N} \Psi^*(\vec{r}, \vec{r_2}, \vec{r_3}, \ldots, \vec{r_N})\Psi(\vec{r}, \vec{r_2}, \vec{r_3}, \ldots, \vec{r_N}) \tag{2}$$

Further, we can arrive at a definition for a density operator that yields expectation value in 2. One can check that the following operator does the trick:

$$\widehat{n}(\vec{r}) = \sum_i^N \delta(\vec{r} - \vec{r_i}) \tag{3}$$

Now, we can write the expectation of energy as, from the Hohenberg-Kohn theorem:

$$E[n] = F[n] + \int V(\vec{r})n(\vec{r})dr^3 \tag{4}$$

Where the $F[n]$ is a *universal* functional of density.

To further gain an intuition about the nature of $F[n]$, we can defer to the *constrained search* formalism of DFT, which gives the $F[n]$ as

$$F[n] = \min_{\{\Psi | \langle \widehat{n}(r) \rangle = n(r)\}} \langle \Psi | \widehat{T} + \widehat{H}_{e-e} | \Psi \rangle \tag{5}$$

Even otherwise, te $F[n]$ has a similar interpretation. The key takeaway, though, is that the exact form of $F[n]$ is difficult to obtain explicitly as a function of n. Even though the Hohenberg-Kohn theorems make such a representation possible in theory,

- A given density n fixes the $V(\vec{r})$, by HK.
- This fixes all terms in the many-body Schrödinger equation, which is solved to give Ψ
- The above [5] expectation value is then taken.

there is no prescription for the first step, nor a general or easy way to deal with the second.

One way to circumvent this difficulty is to write the unknown $\langle \widehat{H}_{e-e} \rangle$ at least partly as a funcional of density. We expect a large contribution to this to come from a simple couloumbic-Hartree like term $\int\int \frac{e^2 n(\vec{r}) n(\vec{r}\,')}{2|\vec{r}-\vec{r}\,'|} d\vec{r} d\vec{r}\,'$. All other effects are clubbed in under the $E_{xc}[n]$ or the exchange-correlation energy.

Now, the real crowning glory of DFT is what can be done using the *Kohn-Sham ansatz*, which states that the correct ground state density of the full interacting system is *exactly* the same as the ground state density of some unknown, non-interacting system. Based on this (details have been skipped), we can reduce the solution of the difficult problem of varying over the $n(\vec{r})$ into solving the self consistent Schrödinger equation:

$$[-\frac{\hbar^2}{2m}\nabla^2 + V_{hartree} + V_{xc} + V_{ext}]\Psi = \epsilon_o \Psi \tag{6}$$

Here, the term $V_{har.}$ acts as an effective electrostatic potential felt by an electron and corresponds to a similar term in the Hartree-Fock treatment. Explicitly, it is given by:

$$V_{har.}(\vec{r}\,') = \int dr' \frac{e^2 n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \tag{7}$$

All of the difficulty has thus been shoved under the carpet in the form of the term V_{xc}. This includes, something like the Hartree exchange effects and other unknown effects that arise from the fact that we haven't assumed a slater determinant ground state. We must next deal with this. Using adiabatic continuation, we get:

$$\begin{aligned} E(1) - E(0) &= \int_0^1 \langle \Psi(\lambda) | \widehat{H}_{e-e} | \Psi(\lambda) \rangle d\lambda + \int_0^1 d\lambda \int \frac{\partial V(r,\lambda)}{\partial \lambda} \langle \hat{n}(r) \rangle dr \\ &= \int_0^1 d\lambda \left\langle \sum_{i<j}^{N} U(\hat{r_i}, \hat{r_j}) \right\rangle + \int [V(\vec{r},1) - V(\vec{r},0)] n(\vec{r}) d\vec{r} \\ &= \int_0^1 d\lambda \int\int d\vec{r} d\vec{r}\,' \frac{e^2}{2|\vec{r}-\vec{r}\,'|} \frac{\left\langle \sum_{i,j}^{N} \delta(\hat{r_i} - \vec{r}) \delta(\hat{r_j} - \vec{r}\,') \right\rangle}{n(\vec{r}) n(\vec{r}\,')} + 2^{\text{nd}} \text{ term} \end{aligned} \tag{8}$$

What