Computational Methods for Materials

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Contents

1 References 1

2 Introduction 2

3 Density Functional Theory (DFT) 2
   3.1 Overview ........................................... 2
   3.2 Procedure ........................................... 4

4 Density Functional Perturbation Theory (DFPT) 5
   4.1 Overview ........................................... 5
   4.2 Procedure ........................................... 6

5 Phonon Calculations 8
   5.1 Hellmann-Feynman Theorem ......................... 8
   5.2 The Quasi-Harmonic Approximation ................. 8
   5.3 Momentum Space Formalism ......................... 9

6 Electron-Phonon Coupling 11
   6.1 Phonon Linewidth ................................. 11
   6.2 Superconducting Critical Temperature ............ 12
1 References


2 Introduction

Many thermodynamic properties can be calculated from the free energy of a material:

\[ F = -k_B T \ln(Z), \]

where \( Z \) is the partition function of the system, defined as:

\[ Z = \sum_n e^{-E_n/k_B T}. \]

However, in order to calculate the partition function, \( Z \), information about the quantum mechanical energies, \( E_n \) must be known. Pines and Nozierres argue in their "Theory of Everything" paper, that a material’s energies can be determined from the following global Hamiltonian:

\[ H = \sum_i \frac{p_i^2}{2m_i} + \sum_\alpha \frac{p_\alpha^2}{2M_\alpha} + e^2 \sum_{i,j} \frac{1}{|r_i - r_j|} + e^2 \sum_{\alpha,\beta} Z_\alpha Z_\beta \frac{1}{|r_\alpha - r_\beta|} + e^2 \sum_{i,\alpha} Z_\alpha \frac{1}{|r_i - r_\alpha|}. \]

However, this equation is intractable for large systems - making the exact ground state wavefunction and energy unobtainable in that limit. The first step taken towards solving large many body systems was the Hatree-Fock method, which effectively simplifies the Hamiltonian - eliminating the ion-ion interaction - and applies an anti-symmetric wavefunction \textit{a priori} in order to correctly model exchange behavior. These wavefunctions are represented as Slater Determinants:

\[ \Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{pmatrix} \phi_1(r_1) & \phi_1(r_2) \\ \phi_2(r_1) & \phi_2(r_2) \end{pmatrix} \]

which generalizes intuitively for \( N \) particles. Varying the parameters of each term and finding the minimum energy yields the ground state. However, this method also becomes computationally expensive for large systems. It is clear that a different approach must be pursued.

3 Density Functional Theory (DFT)

3.1 Overview

DFT computes a material’s ground state electronic \textit{density}. It relies on the Hohenberg-Kohn theorem, which states that every Hamiltonian has a unique electronic ground state density:

\[ \Psi_r \leftrightarrow n_r. \]
\[ E = F[n_r], \]

where \( F[n_r] \) is a functional of electronic density, \( n_r \). The exact form of \( F[n_r] \) is unknown, so, in practice, the Kohn-Sham ansatz is applied. This maps the many-body system to a fictitious non-interacting system:

\[ n_r^I \leftrightarrow n_r^{NI}, \]

which allows the electronic density to be expressed in terms of independent (single particle) basis states, with the following single-particle Hamiltonian:

\[ \left( -\frac{1}{2}\nabla^2 + v_{eff}(r) \right) \phi_i = \epsilon_i \phi_i. \]

The effective potential, \( v_{eff}(r) \), is expressed as independent functionals of electronic density:

\[ v_{eff}(r) = v_{ie}[n_r] + v_{ee}[n_r] + v_{xc}[n_r]. \]

The nuclear term, \( v_{n}[n_r] \), is often provided as a ‘pseudopotential’, which screens the attractive ions with the core electrons. The electron-electron interaction term, \( v_{e-e}[n_r] \), which often depends only on the material’s valence electrons, takes the form of the long-range Coulomb interaction. And the exchange-correlation term, \( v_{xc}[n_r] \), which represents the effects of Pauli exclusion, is approximated - as an exact solution does not exist. A standard approximation is the local density approximation (LDA), which assigns \( V_{xc}[n_r] \) to the energy of a homogenous electron gas at that specific point in space:

\[ V_{xc}^{LDA}[n_r] = \int \int n_r \epsilon_{xc}(n) n_r d^3r d^3r', \]

where

\[ v_{xc}[n_r] = \frac{\delta V_{xc}^{LDA}[n_r]}{\delta n_r}. \]

Computationally, \( n_r \) is constructed from plane wave basis kets, and \( v_{eff}(r) \) is calculated from \( n_r \) as described above. The single-particle Hamiltonian is then solved for the N independent states, and this solution is used to calculate a new density. The process is iterated until self-consistency. Computing the energy with DFT is a 3-dimensional problem, whereas solving the Hamiltonian for an exact solution is a 3N-dimensional problem. This gives DFT a distinct computational advantage over other ‘brute force’ methods.
3.2 Procedure

The self-consistency process for a DFT calculation is as follows.

1. Trial wavefunctions are generated using a basis set - in our case planewaves:

\[ |\phi_i\rangle = \sum_k |k\rangle \langle k|\phi_i\rangle, \]

\[ \langle r|\phi_i\rangle = \sum_k (k|\phi_i\rangle e^{ikr}, \]

\[ \phi_i(r) = \sum_k \phi_i(k)e^{ikr}. \]

2. Determine the electronic density:

\[ n_r = \sum_i \int d^3r \langle \phi_i|\langle r|\phi_i\rangle, \]

\[ n_r = \sum_i \int d^3r \phi_i^*(r)\phi_i(r). \]

3. Determine the effective potential:

\[ v_r = Z_i \int d^3r' \frac{n_{r'}}{|r - r'|} + e^2 \int d^3r' \frac{n_{r'}}{|r - r'|} + v_{xc}[n_r]. \]

4. Solve the single-particle Hamiltonian for new kets and energies:

\[ \langle \phi_i| (\mathcal{T} + v_r - \epsilon_j) |\phi_i\rangle = 0, \]

\[ \langle \phi_i|\phi_j\rangle = \delta_{ij}. \]

5. Return to Step 2 and iterate until self consistency.
4 Density Functional Perturbation Theory (DFPT)

4.1 Overview

Density Functional Perturbation Theory (DFPT) treats lattice fluctuations as perturbative (linear) corrections to the ground state:

\[ v_{\text{eff}}^r \rightarrow v_0^r + \delta v_r, \]
\[ n_r \rightarrow n_0^r + \delta n_r. \]

where \( n_0^r \) and \( v_0^r \) are the unperturbed density and effective potential, respectively, and \( \delta n_r \) and \( \delta v_r \) are the perturbative corrections. The corrected Kohn-Sham Hamiltonian is then written as:

\[ H = H_0^i + H_i', \]
\[ H_0^i = T^0_e + v_0^r, \]
\[ H_i' = \delta v_r. \]

DFPT follows the same procedure as DFT, using the perturbed density to construct the perturbed effective potential - and then solving for the single-particle Kohn-Sham correction term, \( |\Delta \phi_i\rangle \). This procedure is described more completely in the Section below.

\[ |\psi_i\rangle = |\phi_0^i\rangle + |\Delta \phi_i\rangle, \]

\[ (H_i^0 + H_i')(|\phi_0^i\rangle + |\Delta \phi_i\rangle) = (\epsilon_i^0 + \Delta \epsilon_i)(|\phi_0^i\rangle + |\Delta \phi_i\rangle), \]

which simplifies to:

\[ (H_i^0 - \epsilon_i^0) |\Delta \phi_i\rangle = -(H_i' - \Delta \epsilon_i) |\phi_i\rangle^0. \]

This can be expressed in matrix form as:

\[
\begin{pmatrix}
0 & H_i^0 - \epsilon_i^0 \\
(H_i' - \Delta \epsilon_i) & 0
\end{pmatrix}
\begin{pmatrix}
|\phi_0^i\rangle \\
|\Delta \phi_i\rangle
\end{pmatrix} = 0.
\]

Standard numerical methods are used to diagonalize and solve this matrix equation, generating the states and energies.
4.2 Procedure

As noted previously, the DFPT procedure is analogous to the DFT procedure. Please note that derivations for both \( \delta n_r \) and \( \delta v_r \) are provided in Appendix A.

1. Solve for ground state static kets, \( |\phi^0_i\rangle \), using the DFT methods presented above.

2. Compute the linear corrections to these kets, \( |\Delta \phi_i\rangle \), using plane wave basis sets:

\[
|\psi_i\rangle = |\phi^0_i\rangle + |\Delta \phi_i\rangle
\]
\[
|\psi_i\rangle = \sum_k |k\rangle \langle k| \phi^0_i + \sum_{k'} |k'\rangle \langle k'| \Delta \phi_i ,
\]
\[
\langle r|\psi_i\rangle = \sum_k \langle k| \phi^0_i \rangle e^{ikr} + \sum_{k'} \langle k'| \Delta \phi_i \rangle e^{ik'r} ,
\]
\[
\psi_i(r) = \sum_k \phi^0_i(k)e^{ikr} + \sum_{k'} \Delta \phi_i(k')e^{ik'r}.
\]

3. Compute the perturbed density using these kets:

\[
n_r = n^0_r + \delta n_r ,
\]
\[
n_r = \sum_i (|\phi^0_i\rangle + |\Delta \phi_i\rangle) : (|\phi^0_i\rangle + |\Delta \phi_i\rangle) ,
\]
\[
n_r = \sum_i <\phi^0_i|\phi^0_i> + <\phi^0_i|\Delta \phi_i> + <\Delta \phi_i|\phi^0_i> + h.o.,
\]
\[
n_r = \sum_i <\phi^0_i|\phi^0_i> + 2 \cdot \sum_i <\phi^0_i|\Delta \phi_i> ,
\]
\[
n_r = \sum_i \int d^3r \langle \phi^0_i|r\rangle \langle r|\phi^0_i\rangle + 2 \sum_i \int d^3r \langle \phi^0_i|r\rangle \langle r|\Delta \phi_i\rangle ,
\]
\[
n_r = \sum_i \int d^3r \phi^0_i(r) \phi^0_i(r) + 2 \sum_i \int d^3r \phi^{0*}_i(r) \Delta \phi_i(r).
\]

4. Compute the perturbed effective potential from this density:

\[
v_r = v^0_r + \delta v_r ,
\]
\[
v_r^0 = Z_i \int d^3 \mathbf{r}' \frac{n_r^0}{| \mathbf{r} - \mathbf{r}' |} + e^2 \int d^3 \mathbf{r}' \frac{n_r^0}{| \mathbf{r} - \mathbf{r}' |} + v_{xc}[n_r^0],
\]

\[
\delta v_r = Z_i \int d^3 \mathbf{r}' \frac{\delta n_r'}{| \mathbf{r} - \mathbf{r}' |} + e^2 \int d^3 \mathbf{r}' \frac{\delta n_r'}{| \mathbf{r} - \mathbf{r}' |} + \delta v_{xc}[\delta n_r].
\]

5. Solve the perturbed Hamiltonian for new kets and energies, \( \delta v \).

\[
(T_0^0 + v_r^0 - \epsilon_i^0) | \Delta \phi_i \rangle = -(\delta v_r - \Delta \epsilon_i) | \phi_i^0 \rangle.
\]

6. Return to Step 2 and iterate until self consistency.

It is important to note that DFPT requires self-consistent updates to the corrected term, \( \Delta \phi_i \), only - as the ground state (static) term \( \phi_i^0 \), is determined in Step 1. Further simplifications to electronic density are applied for metals, insulators, and semiconductors, respectively. These corrections are discussed in later sections.
5 Phonon Calculations

5.1 Hellmann-Feynman Theorem

The Hellmann-Feynman Theorem states that the change in energy of a system with respect to a generalized coordinate can be expressed as the expectation value of the system’s Hamiltonian differentiated by that coordinate:

\[
\frac{\partial \epsilon}{\partial r_i} = \langle \Phi | \frac{\partial H}{\partial r_i} | \Phi \rangle,
\]

\[
F_i = -\frac{\partial \epsilon}{\partial r_i}.
\]

This theorem provides motivation for the direct calculation of the Hessian Matrix - \( \frac{\partial^2 \epsilon}{\partial r_i \partial r_j} \) - from which information about the crystalline dynamics can be obtained.

5.2 The Quasi-Harmonic Approximation

Lattice vibrations can be quantified using the quasi-harmonic approximation, which assumes each ion moves about a local harmonic (parabolic) minimum - mimicking a linear restoring force:

\[
F = -kx,
\]

\[
H_{vib} = \frac{p^2}{2m} + \frac{1}{2}kx^2.
\]

The solution to this equation is oscillatory, with frequency being defined via the 2nd spatial derivative:

\[
\frac{\partial^2 H_{vib}}{\partial^2 x} = k = \frac{\partial^2 V(x)}{\partial^2 x},
\]

which naturally yields a constant with units \( kg/s^2 \). Scaling this expression inversely by mass eliminates the mass dependence:

\[
\frac{1}{m} \frac{\partial^2 V(x)}{\partial^2 x} = \omega^2.
\]

For a many body system, the left hand side of this equation is a 2 dimensional matrix, known as the Hessian Matrix (matrix of second derivatives), with equal dimensions: \((\text{number of degrees of freedom}) \cdot (\text{number of atoms in the system})\).
unit cell). For example, a 3-dimensional crystal with N atoms in its unit cell would have dimensions 3N x 3N, with each matrix term being defined by:

$$\frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V(x)}{\partial x_i \partial x_j} = k_{ij}.$$ 

Since the right hand side ($\omega^2$) is constant, this matrix equation becomes an eigenvalue problem. The eigenvalues (modes) are determined by solving the determinant:

$$\det \left[ \frac{1}{m} \frac{\partial^2 V(x)}{\partial^2 x} - \omega^2 \right] = 0,$$

and then used to construct the corresponding eigenvectors. The solutions have the form:

$$\vec{\omega} = (\omega_1^1, \omega_1^2, \omega_1^3, ..., \omega_N^1, \omega_N^2, \omega_N^3),$$

$$\vec{e} = (e_1^1, e_1^2, e_1^3, ..., e_N^1, e_N^2, e_N^3).$$

The eigenvectors are also normalized by the mass of the corresponding atom. For clarity, they can be written as:

$$\vec{e} = (\frac{e_1^1}{\sqrt{m_1}}, \frac{e_1^2}{\sqrt{m_1}}, \frac{e_1^3}{\sqrt{m_1}}, ..., \frac{e_N^1}{\sqrt{m_N}}, \frac{e_N^2}{\sqrt{m_N}}, \frac{e_N^3}{\sqrt{m_N}}).$$

Typically, the Hessian Matrix is determined first via DFPT, and a secondary software is utilized to diagonalize and solve for the normal modes (i.e. eigenvalues). The key to this whole procedure is the direct calculation of the Hessian Matrix via DFPT, which is explicitly represented as:

$$\frac{\partial^2 V_{SCF}}{\partial x_i \partial x_j} = \int d^3 r \delta n_r \delta v_r + \int d^3 r \delta n_r \frac{\partial^2 V_{SCF}}{\partial x_i \partial x_j} + \frac{\partial^2 V_{ion-ion}}{\partial x_i \partial x_j}.$$ 

The final term represents the ion-ion interaction, and is often approximated to zero since electron screening makes its magnitude negligible. The first term consists of electronic contributions, and the second term consists of changes in the harmonic potential as individual atoms are moved in various directions.

### 5.3 Momentum Space Formalism

Given that DFT is implemented on infinite, periodic systems, it is often more convenient to work with Fourier transforms of real-space quantities. Consequently, the eigenvalue problem becomes:

$$\left( \omega_q^2 \right)^2 = \frac{1}{\sqrt{N}} \sum_a e^{i a q} \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V_{SCF}}{\partial x_i \partial x_j}$$
in momentum ($q$) space. Here, $i$ and $j$ represent the different atoms within each unit cell, and $a$ represents the specific unit cell within the entire crystal. Since there are $N$ total atoms within a unit cell, the entire quantity is normalized by $\sqrt{N}$. Of course, the corresponding momentum-space eigen-vectors $e_{i}^{\nu q}$ are solutions to this equation:

\[
(\omega_{q}^{\nu})^{2} e_{i}^{\nu q} = \frac{1}{\sqrt{N}} \sum_{a} e^{iaq} \frac{1}{\sqrt{m_{i}m_{j,a}}} \frac{\partial^{2} V_{SCF}}{\partial x_{i} \partial x_{j}} e_{i}^{\nu q}.
\]

It should be noted that the $q$ perturbations can be of arbitrary length and direction - such that the periodicity of a phonon displacement can be of arbitrary size. This eliminates the need, from a calculations standpoint, for supercells. Moreover, the $q$-point sampling of the BZ need only be as dense as the k-point sampling for a traditional DFT calculation.
6 Electron-Phonon Coupling

6.1 Phonon Linewidth

Electron phonon coupling seeks to quantify changes within the electronic spectrum due to atomic displacements. Specifically, when an atom is moved from its equilibrium position, the electronic energies within the unit cell change, and mixing between different momentum states occurs. The electron scattering is therefore coupled to the lattice vibrations. The electron-phonon scattering process can be described by Fermi’s Golden Rule:

$$\Gamma_{i \rightarrow j} = \frac{2\pi}{\hbar} |\langle i|\delta v|f \rangle|^2 [f(\epsilon_f) - f(\epsilon_i)] \delta(\epsilon_f - \epsilon_i + \hbar \omega),$$

where $f(\epsilon_f)$ and $f(\epsilon_i)$ represent Fermi factors for the empty and filled states, respectively, and the delta function constrains the interaction to be within $+/- \ h \omega$. Since the Debye temperature of most materials is on the order of thousands of degrees, all scattering (in this scenario) occurs around the Fermi surface. Moreover, by summing all scattering states within this range, the full expression becomes:

$$\gamma_{q\nu} = \frac{2\pi}{\hbar N_k} \sum_k \sum_{m,n} |\langle k, m|\delta v^{q\nu}|k + q, n \rangle|^2 [f(\epsilon_f) - f(\epsilon_i)] \delta(\epsilon_{k+q,n} - \epsilon_{k,m} + \hbar \omega_{q\nu}),$$

where $m$ and $n$ represent branch indices of the electronic states, and $\nu$ represents branch indices of the phonon states. This sum, scaled inversely by the total number of possible scattering states, is the phonon linewidth, a probability attempt frequency with units of inverse seconds. Often, $\gamma_{q\nu}$ is simplified further since the difference in Fermi factors is so close to a delta function, i.e.:

$$\frac{f(\epsilon_f) - f(\epsilon_i)}{\hbar \omega_{q\nu}} = \delta(\epsilon_f - \epsilon_i),$$

$$f(\epsilon_f) - f(\epsilon_i) = \hbar \omega_{q\nu} \delta(\epsilon_f - \epsilon_i).$$

Since both energies must equal in this approximation, all scattering is constrained to the Fermi surface, simplifying the expression to:

$$\gamma_{q\nu} = \frac{2\pi \omega_{q\nu}}{N(\epsilon_F)} \sum_k \sum_{m,n} |\langle k, m|\delta v^{q\nu}|k + q, n \rangle|^2 \delta(\epsilon_{k,m} - \epsilon_F) \delta(\epsilon_{k+q,n} - \epsilon_F).$$
6.2 Superconducting Critical Temperature

The phonon linewidth is a property that can be experimentally confirmed. Furthermore, from this linewidth, properties such as superconducting $T_c$ can be calculated. The only challenging part is calculating the momentum-dependent terms of the electron-phonon coupling (scattering) matrix:

$$g_{k+q,k}^{q\nu,m,n} = \left( \frac{\hbar}{2\omega_{q\nu}} \right)^{1/2} \langle k, m | \delta \varphi_{q\nu} | k + q, n \rangle.$$  

However, the terms needed to calculate these elements are obtained via DFPT, where the states are the self-consistent solutions to the perturbed Kohn-Sham Hamiltonian, and the mixing potential is the linear Kohn-Sham correction:

$$\delta \varphi_{q\nu} = \frac{1}{\sqrt{N}} \sum_a \sum_i \frac{\partial V_{KS}}{\partial x_i} e_i \epsilon_{aq}.$$  

The sum over $a$ (the various unitcells within our infinite solid) and $i$ (the specific atom within our starting unitcell) represents a Fourier transform of the perturbation potential, and $e_{aq}$ is the phonon eigenvector for that specific $q$-perturbation - which specifies the displacement pattern for that phonon mode. This is normalized by the number of unitcells ($N$) in the sum. A dimensionless coupling constant, $\lambda_{q\nu}$, can then be obtained by scaling the phonon linewidth by the vibrational mode:

$$\lambda_{q\nu} = \frac{\gamma_{q\nu}}{\omega_{q\nu}},$$

and summing over all possible modes:

$$\lambda = \sum_{q\nu} \frac{\gamma_{q\nu}}{\omega_{q\nu}},$$

which in the continuous limit is expressed as:

$$\frac{1}{N(\epsilon_F)} \sum_{q\nu} \frac{\gamma_{q\nu}}{\omega_{q\nu}} \delta(\omega - \omega_{q\nu}) \to 2 \int_0^{\hbar \omega_D} d\omega \frac{\alpha^2 F(\omega)}{\omega}.$$  

The factor of 2 represents degeneracies from both spins - which up to this point have been ignored. $\alpha^2 F(\omega)$ is essentially a re-representation of the phonon linewidth, and is known as the Eliashberg spectral function, after the scientist who developed the theory. It is important to note that the accuracy of $\lambda$ depends directly on the granularity with which the integral
is computed. Since computing DFPT with a dense q-point grid can be computationally intensive - the $\omega$ integration over the Brillouin zone can be taxing. Various interpolation techniques exist to utilize sparse q-grids - with varying degrees of success. Of course, the point of calculating the coupling constant $\lambda$ is to determine the critical temperature:

$$T_c = \frac{\omega_D}{1.2} \exp\left(\frac{1.04(1 + \lambda)}{\lambda + (1 - 0.62\lambda)\mu^*}\right).$$

This expression is analogous to the expression derived in BCS theory:

$$k_B T_c \propto \hbar \omega_D e^{\frac{1}{\sqrt{N(G_F)}}},$$

with a non-constant interaction potential, $V$, (i.e. with a momentum dependent electron-phonon coupling matrix). Note, in the former expression, $\mu^*$ represents the Coulomb repulsion between two electrons in a Cooper pair, which is of course offset by the attractive interaction (i.e. coupling constant). $\mu^*$ is a hyperparameter whose value is guessed. Integrating momentum dependence into the BCS interaction potential was formulated by Eliashberg and Migdal, and this theory largely bears their name.
7 Appendix A

DFT Functionals

\[ v_{e-i}(r) = \frac{\delta}{\delta r} \int d^3 r \int d^3 r' e^{2n(r)Z_i n(r')} \frac{n(r')}{|r - r'|} \]

\[ v_{e-e}(r) = \frac{\delta}{\delta r} \int d^3 r \int d^3 r' e^{2n(r)n(r')} \frac{n(r)}{|r - r'|} \]

\[ V_{xc}^{GGA}[n_r] = \int \int n_r \epsilon_{xc}(n, \delta n)n_r d^3 r d^3 r'. \]

Density Perturbation  The procedure for solving the perturbed electronic density is analogous to for standard DFT. Electronic density is typically expressed as

\[ n(r) = \langle \psi | \psi \rangle, \]

\[ n(r) = \sum_i |a_i|^2 \langle \phi_i | \phi_i \rangle, \]

\[ n(r) = \int d^3 r \sum_i |a_i|^2 \langle \phi_i | r \rangle \langle r | \phi_i \rangle, \]

\[ n(r) = \int d^3 r \sum_i |a_i|^2 \phi_i^*(r) \phi_i(r). \]

A change in this density due to an atomic displacement can be expressed as the derivative of this density with respect to \( r \):

\[ \frac{\delta n(r)}{\delta r'} = \frac{\delta}{\delta r'} \int d^3 r \sum_i |a_i|^2 \phi_i^*(r) \phi_i(r) \delta(r - r'). \]

The right hand side can be simplified by:

\[ \frac{\delta n(r)}{\delta r} = \sum_i |a_i|^2 \phi_i^*(r) \phi_i(r) \frac{\delta \phi_i(r)}{\delta r} + \phi_i^* \frac{\delta \phi_i(r)}{\delta r}. \]

\[ \delta n(r) = \sum_i |a_i|^2 (\delta \phi_i^* \phi_i + \phi_i^* \delta \phi_i) \]

\[ \delta n(r) = 2 \sum_i |a_i|^2 \phi_i^* \delta \phi_i, \]

where

\[ \delta \phi_i(r) = \langle r | \Delta \phi_i \rangle. \]
Expanding this out with the first-order correction to $|\Delta \phi_i\rangle$ yields:

$$
\delta n(r) = 4 \sum_{i=1}^{N/2} \sum_{j=i}^{N/2} \frac{\langle \phi_i | \delta v | \phi_i \rangle}{\epsilon_j - \epsilon_i} \phi_j^*(r) \phi_i(r).
$$

**Potential Perturbation**  
Our correction to the effective potential, $\delta v$, is applied logically:

$$
v_{\mathrm{eff}}[n_r] = v_{\ie}[n_r] + v_{\ce}[n_r] + v_{\xc}[n_r],
$$

$$
\frac{\delta v_{\mathrm{eff}}[n_r]}{\delta n_r} = \frac{\delta v_{\ie}[n_r]}{\delta n_r} + \frac{\delta v_{\ce}[n_r]}{\delta n_r} + \frac{\delta v_{\xc}[n_r]}{\delta n_r},
$$

$$
\delta v_{\mathrm{eff}}[n_r] = \frac{\delta v_{\ie}[n_r]}{\delta n_r} \delta n_r + \frac{\delta v_{\ce}[n_r]}{\delta n_r} \delta n_r + \frac{\delta v_{\xc}[n_r]}{\delta n_r} \delta n_r.
$$

Where each term equals the following:

$$
\frac{\delta v_{\ie}[n_r]}{\delta n_r} \delta n_r = Z_i \int d^3r' \frac{\delta n_{r'}}{|r - r'|},
$$

$$
\frac{\delta v_{\ce}[n_r]}{\delta n_r} \delta n_r = e^2 \int d^3r' \frac{\delta n_{r'}}{|r - r'|},
$$

$$
\frac{\delta v_{\xc}[n_r]}{\delta n_r} \delta n_r = \delta v_{\xc}[n_r].
$$

So our perturbed potential can be expressed as:

$$
\delta v_{\mathrm{eff}} = Z_i \int d^3r' \frac{\delta n_{r'}}{|r - r'|} + e^2 \int d^3r' \frac{\delta n_{r'}}{|r - r'|} + \delta v_{\xc}[n_r].
$$

Again, the ion-ion term is not included. This term is discussed at the end.
**Hessian Matrix** A derivative of the Hellmann-Feynman force provides the Hessian Matrix. The Hessian is often said to contain 'Force Constants,' since

\[ V(x) = \frac{1}{2} k x^2, \]

and

\[ \frac{\partial^2 V(x)}{\partial^2 x} = k. \]

The specific form of each element in the Hessian Matrix is:

\[
\frac{\partial^2 V(\vec{r})}{\partial r_i \partial r_j} = \int d^3 r \frac{\partial n_r}{\partial r_j} \frac{\partial v_{ie}}{\partial r_i} + \int d^3 r n_r \frac{\partial^2 v_{ie}}{\partial r_i \partial r_j} + \frac{\partial^2 v_{ii}}{\partial r_i \partial r_j}.
\]

The first term depends on the change in electronic density due to an atomic perturbation, which is the \( \delta n_r \) term calculated via DFPT, and the change in the electron-ion interaction due to this perturbation. The second term depends on the unperturbed electronic density, \( n_r \), and the second derivative of the electron-ion interaction. The final term represents the second derivative of the ion-ion interaction, whose form is again known explicitly. The position indices, \( i \) and \( j \), correspond to the different atoms within the unit cell.