Appendix A

Perturbation theory

This section aims to recall the most notable results of the perturbation theory.

This section is mainly based on *"MAPR 2451: Atomistic and nanoscopic simulations"* taught by Pr. G.-M. Rignanese [55] and on the presentation about *"Lattice responses to atomic displacements and static electric fields"* of Prof. G.-M. Rignanese in Zurich [59].

A.1 Expansion of the Schrödinger equation

Let us assume that the ground state solutions are known for a system described by its time-independent Schrödinger equation:

$$H^{(0)} \left| \Psi_i^{(0)} \right\rangle = \varepsilon_i^{(0)} \left| \Psi_i^{(0)} \right\rangle \tag{A.1}$$

with the normalization condition:

$$\left\langle \Psi_i^{(0)} \middle| \Psi_i^{(0)} \right\rangle = 1 \tag{A.2}$$

and where $\left| \Psi_i^{(0)} \right\rangle$ are the eigenfunctions of the Schrödinger equation which form an orthogonal basis set.

A known perturbation is introduced in the external potential and is characterized by a small parameter λ, such that the external potential is now given by:

$$V_{\text{ext}}(\lambda) = V_{\text{ext}}^{(0)} + \lambda V_{\text{ext}}^{(1)} + \lambda^2 V_{\text{ext}}^{(2)} + ... \tag{A.3}$$

We now want to obtain the solutions of the perturbed Schrödinger equation:

$$H(\lambda) \left| \Psi_i(\lambda) \right\rangle = \varepsilon_i(\lambda) \left| \Psi_i(\lambda) \right\rangle \tag{A.4}$$

with the normalization condition:

$$\left\langle \Psi_i(\lambda) \middle| \Psi_i(\lambda) \right\rangle = 1 \tag{A.5}$$

The basic idea is to write all the quantities that appear in the Schrödinger equation as a perturbation series with respect to this parameter λ:

$$H(\lambda) = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + ... \qquad \text{with } H^{(k)} = \frac{1}{k!} \frac{d^k H}{d\lambda^k} \tag{A.6}$$

$$\varepsilon_i(\lambda) = \varepsilon_i^{(0)} + \lambda \varepsilon_i^{(1)} + \lambda^2 \varepsilon_i^{(2)} + ... \qquad \text{with } \varepsilon_i^{(k)} = \frac{1}{k!} \frac{d^k \varepsilon_i}{d\lambda^k} \tag{A.7}$$

$$\left| \Psi_i(\lambda) \right\rangle = \left| \Psi_i^{(0)} \right\rangle + \lambda \left| \Psi_i^{(1)} \right\rangle + \lambda^2 \left| \Psi_i^{(2)} \right\rangle + ... \qquad \text{with } \left| \Psi_i^{(k)} \right\rangle = \frac{1}{k!} \frac{d^k \left| \Psi_i \right\rangle}{d\lambda^k} \tag{A.8}$$

Inserting equations A.6, A.7, and A.8 into the perturbed Schrödinger equation A.4 gives:

$$\left(H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + ...\right)\left(\left|\Psi_i^{(0)}\right\rangle + \lambda\left|\Psi_i^{(1)}\right\rangle + \lambda^2\left|\Psi_i^{(2)}\right\rangle + ...\right)$$
$$= \left(\varepsilon_i^{(0)} + \lambda\varepsilon_i^{(1)} + \lambda^2\varepsilon_i^{(2)} + ...\right)\left(\left|\Psi_i^{(0)}\right\rangle + \lambda\left|\Psi_i^{(1)}\right\rangle + \lambda^2\left|\Psi_i^{(2)}\right\rangle + ...\right) \tag{A.9}$$

This can be rewritten as:

$$\begin{aligned}
&H^{(0)}\left|\Psi_i^{(0)}\right\rangle + \lambda\left(H^{(0)}\left|\Psi_i^{(1)}\right\rangle + H^{(1)}\left|\Psi_i^{(0)}\right\rangle\right)\\
&+\lambda^2\left(H^{(0)}\left|\Psi_i^{(2)}\right\rangle + H^{(1)}\left|\Psi_i^{(1)}\right\rangle + H^{(2)}\left|\Psi_i^{(0)}\right\rangle\right) + ...\\
&= \varepsilon_i^{(0)}\left|\Psi_i^{(0)}\right\rangle + \lambda\left(\varepsilon_i^{(0)}\left|\Psi_i^{(1)}\right\rangle + \varepsilon_i^{(1)}\left|\Psi_i^{(0)}\right\rangle\right)\\
&+\lambda^2\left(\varepsilon_i^{(0)}\left|\Psi_i^{(2)}\right\rangle + \varepsilon_i^{(1)}\left|\Psi_i^{(1)}\right\rangle + \varepsilon_i^{(2)}\left|\Psi_i^{(0)}\right\rangle\right) + ...
\end{aligned} \tag{A.10}$$

Finally, equating terms in the same power of λ gives rise to the following set of equations:

$$H^{(0)}\left|\Psi_i^{(0)}\right\rangle = \varepsilon_i^{(0)}\left|\Psi_i^{(0)}\right\rangle \qquad 0^{\text{th}} \text{ order} \tag{A.11}$$

$$H^{(0)}\left|\Psi_i^{(1)}\right\rangle + H^{(1)}\left|\Psi_i^{(0)}\right\rangle = \varepsilon_i^{(0)}\left|\Psi_i^{(1)}\right\rangle + \varepsilon_i^{(1)}\left|\Psi_i^{(0)}\right\rangle \qquad 1^{\text{st}} \text{ order} \tag{A.12}$$

$$H^{(0)}\left|\Psi_i^{(2)}\right\rangle + H^{(1)}\left|\Psi_i^{(1)}\right\rangle + H^{(2)}\left|\Psi_i^{(0)}\right\rangle = \varepsilon_i^{(0)}\left|\Psi_i^{(2)}\right\rangle + \varepsilon_i^{(1)}\left|\Psi_i^{(1)}\right\rangle + \varepsilon_i^{(2)}\left|\Psi_i^{(0)}\right\rangle \qquad 2^{\text{nd}} \text{ order} \tag{A.13}$$

Inserting equations A.6, A.7, and A.8 into the normalization condition A.5 gives:

$$\begin{aligned}
&\left\langle\Psi_i^{(0)}\middle|\Psi_i^{(0)}\right\rangle + \lambda\left(\left\langle\Psi_i^{(0)}\middle|\Psi_i^{(1)}\right\rangle + \left\langle\Psi_i^{(1)}\middle|\Psi_i^{(0)}\right\rangle\right)\\
&+\lambda^2\left(\left\langle\Psi_i^{(0)}\middle|\Psi_i^{(2)}\right\rangle + \left\langle\Psi_i^{(1)}\middle|\Psi_i^{(1)}\right\rangle + \left\langle\Psi_i^{(2)}\middle|\Psi_i^{(0)}\right\rangle\right) + ... = 1
\end{aligned} \tag{A.14}$$

Equating terms in the same power of λ gives rise to the following set of equations:

$$\left\langle\Psi_i^{(0)}\middle|\Psi_i^{(0)}\right\rangle = 1 \qquad 0^{\text{th}} \text{ order} \tag{A.15}$$

$$\left\langle\Psi_i^{(0)}\middle|\Psi_i^{(1)}\right\rangle + \left\langle\Psi_i^{(1)}\middle|\Psi_i^{(0)}\right\rangle = 0 \qquad 1^{\text{st}} \text{ order} \tag{A.16}$$

$$\left\langle\Psi_i^{(0)}\middle|\Psi_i^{(2)}\right\rangle + \left\langle\Psi_i^{(1)}\middle|\Psi_i^{(1)}\right\rangle + \left\langle\Psi_i^{(2)}\middle|\Psi_i^{(0)}\right\rangle = 0 \qquad 2^{\text{nd}} \text{ order} \tag{A.17}$$

In order to characterize the perturbed system, the value of the derivatives of the energy spectrum and of the eigenfunctions have to be derived. Once they are determined, the perturbed system is known.

A.2 First-order derivative of the energy $\varepsilon_i^{(1)}$ and the Hellmann-Feynman theorem

Starting from the first-order equation derived from the Schrödinger equation A.12, $\varepsilon_i^{(1)}$ can be derived by multiplying it by $\left\langle\Psi_i^{(0)}\right|$:

$$\left\langle\Psi_i^{(0)}\middle|H^{(0)}\middle|\Psi_i^{(1)}\right\rangle + \left\langle\Psi_i^{(0)}\middle|H^{(1)}\middle|\Psi_i^{(0)}\right\rangle = \left\langle\Psi_i^{(0)}\middle|\varepsilon_i^{(0)}\middle|\Psi_i^{(1)}\right\rangle + \left\langle\Psi_i^{(0)}\middle|\varepsilon_i^{(1)}\middle|\Psi_i^{(0)}\right\rangle \tag{A.18}$$

This equation can be simplified:

- $\varepsilon_i^{(k)}$ can always exit a multiplication between two eigenfunctions:

$$\left\langle \Psi_i^{(0)} \middle| \varepsilon_i^{(0)} \middle| \Psi_i^{(1)} \right\rangle = \varepsilon_i^{(0)} \left\langle \Psi_i^{(0)} \middle| \Psi_i^{(1)} \right\rangle \text{ and } \left\langle \Psi_i^{(0)} \middle| \varepsilon_i^{(1)} \middle| \Psi_i^{(0)} \right\rangle = \varepsilon_i^{(1)} \left\langle \Psi_i^{(0)} \middle| \Psi_i^{(0)} \right\rangle \tag{A.19}$$

- The eigenfunctions form an orthonormal basis:

$$\left\langle \Psi_i^{(k)} \middle| \Psi_j^{(k)} \right\rangle = 1 \text{ if } i = j \tag{A.20}$$

$$= 0 \text{ if } i \neq j \tag{A.21}$$

- Thanks to relation A.11, we have:

$$\left\langle \Psi_i^{(0)} \right| H^{(0)} = \left\langle \Psi_i^{(0)} \right| \varepsilon_i^{(0)} \tag{A.22}$$

Applying these simplifications gives rise to the following equation for the first-order derivative of the energy:

$$\varepsilon_i^{(1)} = \left\langle \Psi_i^{(0)} \middle| H^{(1)} \middle| \Psi_i^{(0)} \right\rangle \tag{A.23}$$

In order to obtain the first-order correction to the energy, the only required quantities are the ground state wavefunctions. Equation A.23 is nothing else than the Hellmann-Feynman theorem which states that the first derivative of the eigenvalue of a Hamiltonian that depends on a parameter λ is given by the expectation value of the derivative of the Hamiltonian [116].

The equation A.12 which links the unknown quantity $\left| \Psi_i^{(1)} \right\rangle$ with the known data could be used to obtain the Sternheimer equation, by gathering all the terms with the same eigenfunctions:

$$\left(H^{(0)} - \varepsilon_i^{(0)} \right) \left| \Psi_i^{(1)} \right\rangle = \left(\varepsilon_i^{(1)} - H^{(1)} \right) \left| \Psi_i^{(0)} \right\rangle \tag{A.24}$$

This equation can be rewritten as a matricial problem with x the unknown $\left| \Psi_i^{(1)} \right\rangle$, A the matrix $\left(H^{(0)} - \varepsilon_i^{(0)} \right)$ and y the data fully characterized $\left(\varepsilon_i^{(1)} - H^{(1)} \right) \left| \Psi_i^{(0)} \right\rangle$:

$$A \cdot x = y \Leftrightarrow x = A^{-1} \cdot y \tag{A.25}$$

As the matrix A is not reversible because there is a value $x = \left| \Psi_i^{(0)} \right\rangle$ for which $A \cdot x = 0$, we have to find another way to solve the Sternheimer equation. One solution is to rewrite the wave functions at the first-order as a linear combination of the orthonormal basis of the unperturbed eigenfunctions:

$$\left| \Psi_i^{(1)} \right\rangle = \sum_j c_{ji}^{(1)} \left| \Psi_j^{(0)} \right\rangle \tag{A.26}$$

Taking back the Sternheimer equation A.24, and multiplying it by $\left\langle \Psi_j^{(0)} \right|$, it gives:

$$\left\langle \Psi_j^{(0)} \middle| \left(H^{(0)} - \varepsilon_i^{(0)} \right) \middle| \Psi_i^{(1)} \right\rangle = \left\langle \Psi_j^{(0)} \middle| \left(\varepsilon_i^{(1)} - H^{(1)} \right) \middle| \Psi_i^{(0)} \right\rangle \tag{A.27}$$

$$\Leftrightarrow \left\langle \Psi_j^{(0)} \middle| \left(\varepsilon_j^{(0)} - \varepsilon_i^{(0)} \right) \middle| \Psi_i^{(1)} \right\rangle = \left\langle \Psi_j^{(0)} \middle| \left(\varepsilon_i^{(1)} - H^{(1)} \right) \middle| \Psi_i^{(0)} \right\rangle \tag{A.28}$$

$$\Leftrightarrow \left(\varepsilon_j^{(0)} - \varepsilon_i^{(0)} \right) \left\langle \Psi_j^{(0)} \middle| \Psi_i^{(1)} \right\rangle = \varepsilon_i^{(1)} \left\langle \Psi_j^{(0)} \middle| \Psi_i^{(0)} \right\rangle - \left\langle \Psi_j^{(0)} \middle| H^{(1)} \middle| \Psi_i^{(0)} \right\rangle \tag{A.29}$$

$$\left(\varepsilon_j^{(0)} - \varepsilon_i^{(0)} \right) c_{ji}^{(1)} = \varepsilon_i^{(1)} \delta_{ji} - \left\langle \Psi_j^{(0)} \middle| H^{(1)} \middle| \Psi_i^{(0)} \right\rangle \tag{A.30}$$

For $j = i$:

$$\left(\varepsilon_i^{(0)} - \varepsilon_i^{(0)}\right) c_{ii}^{(1)} = \varepsilon_i^{(1)} - \left\langle \Psi_i^{(0)} \middle| H^{(1)} \middle| \Psi_i^{(0)} \right\rangle \tag{A.31}$$

$$\Leftrightarrow 0 \cdot c_{ii}^{(1)} = 0 \tag{A.32}$$

$c_{ii}^{(1)}$ is undetermined. In order to continue the derivation of $\left|\Psi_i^{(1)}\right\rangle$, $c_{ii}^{(1)}$ is set to zero. It is called a gauge choice: one good solution is chosen among all the possible solutions.
For $j \neq i$ and $\varepsilon_j^{(0)} \neq \varepsilon_i^{(0)}$:

$$c_{ji}^{(1)} = \frac{\left\langle \Psi_j^{(0)} \middle| H^{(1)} \middle| \Psi_i^{(0)} \right\rangle}{\varepsilon_i^{(0)} - \varepsilon_j^{(0)}} \tag{A.33}$$

Combining equations A.26 and A.33, with $c_{ii}^{(1)} = 0$ gives rise to:

$$\left|\Psi_i^{(1)}\right\rangle = \sum_{j\neq i} c_{ji}^{(1)} \left|\Psi_j^{(0)}\right\rangle = \sum_{j\neq i} \frac{\left\langle \Psi_j^{(0)} \middle| H^{(1)} \middle| \Psi_i^{(0)} \right\rangle}{\varepsilon_i^{(0)} - \varepsilon_j^{(0)}} \left|\Psi_j^{(0)}\right\rangle \tag{A.34}$$

The knowledge of the ground state energies and wave functions gives a direct access to the first-order wave functions. The first-order wave function of the state i depends on the sum of the unperturbed data of all other states j. Equation A.34 shows that the perturbation is influential on the state i if the energy spectrum of the state i is closer to another energy spectrum of a state j.

A.3 Second-order derivative of the energy $\varepsilon_i^{(2)}$

Starting from the second-order equation derived from the Schrödinger equation A.13, $\varepsilon_i^{(2)}$ can be derived by multiplying it by $\left\langle \Psi_i^{(0)} \right|$:

$$\begin{aligned} &\left\langle \Psi_i^{(0)} \middle| H^{(0)} \middle| \Psi_i^{(2)} \right\rangle + \left\langle \Psi_i^{(0)} \middle| H^{(1)} \middle| \Psi_i^{(1)} \right\rangle + \left\langle \Psi_i^{(0)} \middle| H^{(2)} \middle| \Psi_i^{(0)} \right\rangle \\ &= \varepsilon_i^{(0)} \left\langle \Psi_i^{(0)} \middle| \Psi_i^{(2)} \right\rangle + \varepsilon_i^{(1)} \left\langle \Psi_i^{(0)} \middle| \Psi_i^{(1)} \right\rangle + \varepsilon_i^{(2)} \left\langle \Psi_i^{(0)} \middle| \Psi_i^{(0)} \right\rangle \end{aligned} \tag{A.35}$$

$$\varepsilon_i^{(2)} = \left\langle \Psi_i^{(0)} \middle| H^{(2)} \middle| \Psi_i^{(0)} \right\rangle + \left\langle \Psi_i^{(0)} \middle| H^{(1)} - \varepsilon_i^{(1)} \middle| \Psi_i^{(1)} \right\rangle \tag{A.36}$$

Since the energies are real, we can write that:

$$\begin{aligned} \varepsilon_i^{(2)} &= \left\langle \Psi_i^{(0)} \middle| H^{(2)} \middle| \Psi_i^{(0)} \right\rangle + \left\langle \Psi_i^{(0)} \middle| H^{(1)} - \varepsilon_i^{(1)} \middle| \Psi_i^{(1)} \right\rangle \\ &= \left\langle \Psi_i^{(0)} \middle| H^{(2)} \middle| \Psi_i^{(0)} \right\rangle + \left\langle \Psi_i^{(1)} \middle| H^{(1)} - \varepsilon_i^{(1)} \middle| \Psi_i^{(0)} \right\rangle \end{aligned} \tag{A.37}$$

Combining both equalities gives:

$$\varepsilon_i^2 = \left\langle \Psi_i^{(0)} \middle| H^{(2)} \middle| \Psi_i^{(0)} \right\rangle + \frac{1}{2}\left(\left\langle \Psi_i^{(0)} \middle| H^{(1)} - \varepsilon_i^{(1)} \middle| \Psi_i^{(1)} \right\rangle + \left\langle \Psi_i^{(1)} \middle| H^{(1)} - \varepsilon_i^{(1)} \middle| \Psi_i^{(0)} \right\rangle\right) \tag{A.38}$$

Using the expansion of the normalization condition at first-order A.17, we can finally write that:

$$\varepsilon_i^{(2)} = \left\langle \Psi_i^{(0)} \middle| H^{(2)} \middle| \Psi_i^{(0)} \right\rangle + \frac{1}{2}\left(\left\langle \Psi_i^{(0)} \middle| H^{(1)} \middle| \Psi_i^{(1)} \right\rangle + \left\langle \Psi_i^{(1)} \middle| H^{(1)} \middle| \Psi_i^{(0)} \right\rangle\right) \tag{A.39}$$

In order ot obtain the second-order corrections to the energies, the only required quantities are the zeroth- and first-order wave functions.

A.4 Third-order derivative of the energy $\varepsilon_i^{(3)}$

Starting from the third-order equation derived from the Schrödinger equation:

$$\begin{aligned} &H^{(0)} \left| \Psi_i^{(3)} \right\rangle + H^{(1)} \left| \Psi_i^{(2)} \right\rangle + H^{(2)} \left| \Psi_i^{(1)} \right\rangle + H^{(3)} \left| \Psi_i^{(0)} \right\rangle \\ &= \varepsilon_i^{(0)} \left| \Psi_i^{(3)} \right\rangle + \varepsilon_i^{(1)} \left| \Psi_i^{(2)} \right\rangle + \varepsilon_i^{(2)} \left| \Psi_i^{(1)} \right\rangle + \varepsilon_i^{(3)} \left| \Psi_i^{(0)} \right\rangle \end{aligned} \tag{A.40}$$

$\varepsilon_i^{(3)}$ can be derived by multiplying it by $\left\langle \Psi_i^{(0)} \right|$. After some simplifications, it gives the following expression:

$$\begin{aligned} \varepsilon_i^{(3)} = &\left\langle \Psi_i^{(0)} \middle| H^{(3)} \middle| \Psi_i^{(0)} \right\rangle + \left\langle \Psi_i^{(1)} \middle| H^{(1)} - \varepsilon_i^{(1)} \middle| \Psi_i^{(1)} \right\rangle \\ &+ \left\langle \Psi_i^{(0)} \middle| H^{(2)} \middle| \Psi_i^{(1)} \right\rangle + \left\langle \Psi_i^{(1)} \middle| H^{(2)} \middle| \Psi_i^{(0)} \right\rangle \end{aligned} \tag{A.41}$$

A.5 2n + 1 theorem

The 2n+1 theorem states that the knowledge of the n$^{\text{th}}$-order wave functions allows the calculation of the (2n)$^{\text{th}}$ and (2n+1)$^{\text{th}}$ order energy [116].

It has indeed been shown in the previous sections that both the second- and third-order corrections to the energies can be obtained from the first-order wave functions.