8.4: Quantum forces - the Hellmann-Feynman Theorem

For many systems one is often interested in forces as well as energies. If we can write the energy of \( a \) in state \( \langle \phi \rangle \) as \( E = \langle \phi | \hat{H} | \phi \rangle \) and differentiate with respect to some quantity \( \alpha \) then

\[
\frac{dE}{d\alpha} = \langle \frac{d\phi}{d\alpha} | \hat{H} | \phi \rangle + \langle \phi | \frac{d\hat{H}}{d\alpha} | \phi \rangle + \langle \phi | \hat{H} | \phi \rangle
\]

But since \( \hat{H} | \phi \rangle = E | \phi \rangle \) and \( \langle \phi | \phi \rangle = 1 \) for normalisation:

\[
\frac{dE}{d\alpha} = \langle \phi | \frac{d\hat{H}}{d\alpha} | \phi \rangle + E \frac{d}{d\alpha} \langle \phi | \phi \rangle + \langle \phi | \frac{d\hat{H}}{d\alpha} | \phi \rangle
\]

This result is called the **Hellmann-Feynman theorem**: the first differential of the expectation value of the Hamiltonian with respect to any quantity does not involve differentials of the wavefunction.

For example, if \( \langle \phi | \alpha \rangle \) represents the position of a nucleus in a solid, then the force on that nucleus is the expectation value of the force operator \( \langle \frac{d\hat{H}}{d\alpha} | \phi \rangle \). It can be applied to any quantity which is a differential of the Hamiltonian provided the basis set does not change.

Caveat: if we use an incomplete basis set which depends explicitly the positions of the atoms, then we have \( | \phi \rangle = \sum_{n,i} | u_{n,i}(\mathbf{r}) \rangle \). This gives spurious so-called “Pulay” forces if \( \langle \phi | \phi \rangle \) is not an exact eigenstate.