

MOLECULAR PROPERTIES

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Our focus so far has been on computing the electronic energy of a molecule in the absence of an external electric or magnetic field. However, there are far many other molecule properties which can be calculated beyond the energy at a given electronic structure method. Typically, these properties are given by some response to an external stimuli. As a quick example, the dipole moment is the response of the energy with respect to some external field. There are a few properties which are not response properties (transition moments), which determine absorption intensities.

In general, there are typically three methods by which molecular properties are computed:

- Derivatives of the energy
- From perturbation theory
- Derivatives of expectation values (often called propagator methods)

Lets start with a general discussion.

Firstly, lets consider a static picture (no time-dependence anywhere). Assume there is some perturbation \mathbf{P} such that our energy can be expanded in a Taylor Series as

$$\mathcal{E}(\mathbf{P}) = \mathcal{E}(0) + \frac{\partial \mathcal{E}}{\partial \mathbf{P}} \cdot \mathbf{P} + \frac{1}{2} \mathbf{P}^T \cdot \frac{\partial^2 \mathcal{E}}{\partial \mathbf{P}^2} \cdot \mathbf{P} + \dots \quad (1)$$

This will be our building blocks for properties which come from the derivative of the energy (which is also an expectation value). As a specific example, the polarizability tensor is the second derivative of the energy with respect to some external electric field $\mathbf{P} = \mathbf{E}$.

$$\alpha = -\frac{\partial^2 \mathcal{E}}{\partial \mathbf{E}^2} \quad (2)$$

The perturbation approach is similar to what we have seen in recovering dynamical correlation. Collecting terms up to some order λ^n yields the n th order property. Recall that the second-order term can be written as a sum of matrix elements over all excited states as

$$\mathcal{E}^{(2)} = 2 \sum_{i \neq 0} \frac{|\langle \Phi^{(0)} | \hat{\mathbf{P}} | i^{(0)} \rangle|^2}{\mathcal{E}_0^{(0)} - \mathcal{E}_i^{(0)}} \quad (3)$$

Again, the polarizability to some perturbing dipolar electric field (now $\mathbf{P} = \mathbf{r}$ since electric fields interact with the dipole operator), yields

$$\alpha = -2 \sum_{i \neq 0} \frac{|\langle \Phi^{(0)} | \hat{\mathbf{r}} | i^{(0)} \rangle|^2}{\mathcal{E}_0^{(0)} - \mathcal{E}_i^{(0)}} \quad (4)$$

Note that because this requires a summation over all excited states, it is very inefficient for *ab initio* methods. Instead, semi-empirical methods often employ this method to calculate the molecular properties.

Finally, the propagator formulations expands the expectation value of an operator \hat{O} in terms of the perturbation \mathbf{P} as

$$\langle \Psi | \hat{O} | \Psi \rangle = \langle \Psi_0 | \hat{O} | \Psi_0 \rangle + \frac{\partial \langle \Psi | \hat{O} | \Psi \rangle}{\partial \mathbf{P}} \cdot \mathbf{P} + \frac{1}{2} \mathbf{P}^T \cdot \frac{\partial^2 \langle \Psi | \hat{O} | \Psi \rangle}{\partial \mathbf{P}^2} \cdot \mathbf{P} + \dots \quad (5)$$

Again, the molecular polarizability is given by the first-order change in the dipole moment as

$$\alpha = \frac{\partial \langle \Psi | \hat{\boldsymbol{\mu}} | \Psi \rangle}{\partial \mathbf{E}} \quad (6)$$

For dynamical perturbations, one has to use time-dependent perturbation theory. This is a bit tougher to deal with, and can require a good amount of assumptions. We won't discuss these properties here.

1. MOLECULAR PROPERTIES

1.1. External Electric Field. We have some electronic charge distribution $\rho(\mathbf{r})$ and this can interact with an electric potential $\phi(\mathbf{r})$ giving rise to an energy contribution of

$$\mathcal{E} = \int \rho(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} \quad (7)$$

Recall that the electric field is given as the spatial derivative of the electric potential

$$\mathbf{E} = -\frac{\partial \phi(\mathbf{r})}{\partial \mathbf{r}} \quad (8)$$

Furthermore, on the scale of a molecule, an external electric field is typically uniform over the entire molecule which allows us to expand the energy \mathcal{E} in multipole expansion as

$$\mathcal{E} = q\phi - \boldsymbol{\mu} \cdot \mathbf{E} - \frac{1}{2} \mathbf{Q} : \frac{\partial \mathbf{E}}{\partial \mathbf{r}} - \dots \quad (9)$$

where q is the total electric charge, $\boldsymbol{\mu}$ is the electric dipole moment, \mathbf{Q} is the quadrupole moment, etc. Note that the unperturbed dipole and quadrupole moments (in the absence of an electric field), can be calculated as simple expectation values:

$$\boldsymbol{\mu}_0 = -\langle \Psi | \hat{\mathbf{r}} | \Psi \rangle \quad (10)$$

$$\mathbf{Q}_0 = -\langle \Psi | \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}^T | \Psi \rangle \quad (11)$$

Note, that this is only valid when the wave function is fully-variational. In the event that the wave function is not fully-variational, this is called the unrelaxed dipole moment and quadrupole moment since the wave function has not been fully optimized. Often, though it is sufficient, but electron correlation (for example in MP2) might be missed since the dipole moment would be the same as in HF theory!

Note that when there is an external electric field present, this can lead to an induced dipole, quadrupole, etc moments. The dipole moment can thus be expanded as

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \alpha \cdot \mathbf{E} + \frac{1}{2} \mathbf{E}^T \cdot \boldsymbol{\beta} \cdot \mathbf{E} + \dots \quad (12)$$

where we define $\boldsymbol{\mu}_0$ to be the **permanent dipole moment**, $\boldsymbol{\alpha}$ the dipole polarizability, and $\boldsymbol{\beta}$ the first hyper-polarizability, etc.

Because of this, we can write our energy in the presence of an external electric field as

$$\mathcal{E} = q\phi - \boldsymbol{\mu}_0 \cdot \mathbf{E} - \frac{1}{2} \mathbf{Q} : \frac{\partial \mathbf{E}}{\partial \mathbf{r}} - \dots - \frac{1}{2} \mathbf{E}^T \cdot \boldsymbol{\alpha} \cdot \mathbf{E} - \dots \quad (13)$$

Finally, our total electronic energy is expanded in a Taylor series around the homogeneous field \mathbf{E} as

$$\mathcal{E}(\mathbf{E}) = \mathcal{E}(0) + \frac{\partial \mathcal{E}}{\partial \mathbf{E}} \cdot \mathbf{E} + \frac{1}{2} \mathbf{E}^T \cdot \frac{\partial^2 \mathcal{E}}{\partial \mathbf{E}^2} \cdot \mathbf{E} + \dots \quad (14)$$

Recall that by definition, $\boldsymbol{\mu}$ is given as $-\frac{\partial \mathcal{E}}{\partial \mathbf{E}}$. Taking the derivative of Eq. (14), we can write that

$$\boldsymbol{\mu} = -\frac{\partial \mathcal{E}}{\partial \mathbf{E}} - \frac{\partial^2 \mathcal{E}}{\partial \mathbf{E}^2} \cdot \mathbf{E} - \frac{1}{2} \mathbf{E}^T \cdot \frac{\partial^3 \mathcal{E}}{\partial \mathbf{E}^3} \cdot \mathbf{E} - \dots \quad (15)$$

Comparing with the expression for the dipole moment, we can clearly see that

$$\boldsymbol{\mu}_0 = -\frac{\partial \mathcal{E}}{\partial \mathbf{E}} \quad (16)$$

$$\boldsymbol{\alpha} = -\frac{\partial^2 \mathcal{E}}{\partial \mathbf{E}^2} \quad (17)$$

$$\boldsymbol{\beta} = -\frac{\partial^3 \mathcal{E}}{\partial \mathbf{E}^3} \quad (18)$$

One can do similar expansions for the quadrupole moment and associated polarizabilities as energy derivatives.

1.2. External Magnetic Field. Similarly to the external electric field, we can perform a multipole expansion of the energy interacting with an external magnetic field as

$$\mathcal{E} = -\mathbf{m}_0 \cdot \mathbf{B} - \frac{1}{2} \mathbf{B} \cdot \boldsymbol{\xi} \cdot \mathbf{B} - \dots \quad (19)$$

Since the magnetic field is often much smaller than the electric field, we only need to consider the dipole moment interaction (this amounts to ignoring the gradient of the magnetic field terms).

Similarly, we can compute the dipole moment \mathbf{m}_0 for the unperturbed system using an expectation value

$$\mathbf{m}_0 = -\frac{1}{2} \langle \Psi | \hat{\mathbf{L}}_G + g_e \hat{\mathbf{S}} | \Psi \rangle \quad (20)$$

$$\hat{\mathbf{L}}_G = (\hat{\mathbf{r}} - \hat{\mathbf{R}}_G) \times \hat{\mathbf{p}} \quad (21)$$

where $\hat{\mathbf{R}}_G$ is the gauge origin and g_e is a constant approximately equal to 2. Note that it can be seen that for closed-shell system, the spin part will be zero. Furthermore, the angular momentum component will also be zero for non-degenerate wave functions since the $\hat{\mathbf{L}}_G$ is purely imaginary, whereas the wave function is typically real-valued. Hence, it is very rare to find a permanent magnetic moment!

Just like in the electric field case, in the presence of an external magnetic field, it is possible to induce a magnetic dipole moment. Further, the magnetizability, ξ is the equivalent of the electric polarizability (note the macroscopic quantity is called the magnetic susceptibility, χ). By a similar procedure in the electric field case, it can be seen that

$$\mathbf{m}_0 = -\frac{\partial \mathcal{E}}{\partial \mathbf{B}} \quad (22)$$

$$\xi = -\frac{\partial^2 \mathcal{E}}{\partial \mathbf{B}^2} \quad (23)$$

1.3. Nuclear Magnetic Moments. This time, we take our perturbation to be the nuclear magnetic moment \mathbf{I} which arises from the nuclear spin. Unlike in electrons where we typically like to talk about orbital angular momentum and spin as different quantities, for nuclei, we often talk of the total, intrinsic angular momentum (recall that \mathbf{J} quantities) which we label as \mathbf{I} . In general, protons and neutrons are Fermions; thus nuclei with an odd mass number will have a half-integer spin; whereas an even mass number results in an integer spin. It is only these specific isotopes with an odd number of protons and neutrons for which the nuclei can have a non-zero spin and therefore generate a magnetic field. For even number of protons and neutrons, the nuclei (in the ground state) will have zero spin, and thus not produce a magnetic moment. This is why H-NMR is based off of hydrogen with a single proton, and C-NMR is based on carbon-13 (odd number of protons+neutrons).

In general, we can expand the energy like before as

$$\mathcal{E}(\mathbf{I}_1, \mathbf{I}_2, \dots) = \mathcal{E}(0) + \frac{\partial \mathcal{E}}{\partial \mathbf{I}_1} \cdot \mathbf{I}_1 + \frac{\partial \mathcal{E}}{\partial \mathbf{I}_2} \cdot \mathbf{I}_2 + \frac{1}{2} \mathbf{I}_1^T \cdot \frac{\partial^2 \mathcal{E}}{\partial \mathbf{I}_1 \partial \mathbf{I}_2} \cdot \mathbf{I}_2 + \dots \quad (24)$$

Note that the first derivatives vanish since there is nothing for them to interact with. On the other hand, we define $\mathbf{J}_{12} = \frac{\partial^2 \mathcal{E}}{\partial \mathbf{I}_1 \partial \mathbf{I}_2}$ which gives the NMR coupling constant \mathbf{J} .

1.4. Electron Magnetic Moments. In non-relativistic quantum chemistry, our Hamiltonian does not depend on spin. However, electron spins can interact among each other in so called spin-spin interactions. It makes sense however, that singlet states have no net electron spin, and thus do not have any shift in energy. However, for doublet, triplet, etc, we can model the energy shift as follows

$$\mathcal{E}(\mathbf{s}_1, \mathbf{s}_2, \dots) = \mathcal{E}(0) + \frac{\partial \mathcal{E}}{\partial \mathbf{s}_1} \cdot \mathbf{s}_1 + \frac{\partial \mathcal{E}}{\partial \mathbf{s}_2} \cdot \mathbf{s}_2 + \frac{1}{2} \mathbf{s}_1^T \cdot \frac{\partial^2 \mathcal{E}}{\partial \mathbf{s}_1 \partial \mathbf{s}_2} \cdot \mathbf{s}_2 + \dots \quad (25)$$

However, again, the first derivative terms are zero since we require at least a pair of electron spins. Thus,

$$\mathcal{E}(\mathbf{s}_1, \mathbf{s}_2, \dots) = \mathcal{E}(0) + \mathbf{s}_1^T \cdot \mathbf{D}_{12} \cdot \mathbf{s}_2 + \dots \quad (26)$$

where \mathbf{D} is the zero field splitting which lifts the degeneracy of the individual components of a triplet (or higher multiplet).

1.5. Mixed Derivatives. Mixed derivatives are just the cross terms if the energy is expanded in more than one perturbation. Here are just a few.

The change in dipole moment with respect to geometry displacement along a normal coordinate \mathbf{q} is proportional to the IR absorption. Up to some constant,

$$\text{IR intensity} \propto \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{q}}\right)^2 \propto \left(\frac{\partial^2 \mathcal{E}}{\partial \mathbf{R} \partial \mathbf{E}}\right)^2 \quad (27)$$

Of course, in order to calculate the intensities of overtone bands, as well as additional contribution to the fundamental bands, one needs to include higher-order terms.

The intensity of a Raman band is given by the derivative of the polarizability with respect to a normal coordinate:

$$\text{Raman intensity} \propto \left(\frac{\partial \boldsymbol{\alpha}}{\partial \mathbf{q}}\right)^2 \propto \left(\frac{\partial^3 \mathcal{E}}{\partial \mathbf{E}^2 \partial \mathbf{q}}\right)^2 \quad (28)$$

Finally, the NMR shielding tensor σ is given by

$$\text{NMR shielding} \propto \frac{\partial^2 \mathcal{E}}{\partial \mathbf{B} \partial \mathbf{I}} \quad (29)$$

2. ANALYTIC DERIVATIVES

Our task now is to understand how to take these derivatives. That is, how does one compute $\frac{\partial \mathcal{E}}{\partial \mathbf{E}}$? Fortunately, for variational methods, these derivatives will be more straightforward; whereas for non-variational methods, more work will have to be done to recover the exact quantities. Lets first consider the basic issues:

In general, derivative techniques consider the energy is the presence of some perturbation, take the analytical derivative of the energy n times to get the n th-order property, and then let the perturbation strength go to zero. Our energy can be written therefore as

$$\mathcal{E}(\lambda) = \langle \Psi(\lambda) | \hat{H} + \lambda \hat{\mathbf{P}}_1 + \lambda^2 \hat{\mathbf{P}}_2 | \Psi(\lambda) \rangle \quad (30)$$

For the moment, let us suppose that we are considering a variational method such as HF, MCSCF, etc; and we will deal with non-variational methods like MP2 and CC later. Note that the perturbation terms are explicitly written, whereas the wave function depends *implicitly* on the perturbation (through the explicit parameterization: orbitals and CI coefficients).

If one writes down the first derivative with respect to λ ,

$$\frac{\partial \mathcal{E}}{\partial \lambda} = \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \hat{H} + \lambda \hat{\mathbf{P}}_1 + \lambda^2 \hat{\mathbf{P}}_2 \right| \Psi \right\rangle + \langle \Psi | \hat{\mathbf{P}}_1 + 2\lambda \hat{\mathbf{P}}_2 | \Psi \rangle + \left\langle \Psi \left| \hat{H} + \lambda \hat{\mathbf{P}}_1 + \lambda^2 \hat{\mathbf{P}}_2 \right| \frac{\partial \Psi}{\partial \lambda} \right\rangle \quad (31)$$

Now, lets have the perturbation strength go to zero (ie, $\lambda \rightarrow 0$), then

$$\left. \frac{\partial \mathcal{E}}{\partial \lambda} \right|_{\lambda=0} = \langle \Psi(0) | \hat{\mathbf{P}}_1 | \Psi(0) \rangle + 2 \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \hat{H} \right| \Psi(0) \right\rangle \quad (32)$$

Again, the wave function depends on the perturbation implicitly through the variational parameters (orbital coefficients, $\boldsymbol{\kappa}$; CI vector, \mathbf{C}) and AO basis functions (ϕ_μ). In general,

though

$$\frac{\partial \Psi}{\partial \lambda} = \frac{\partial \Psi}{\partial \mathbf{C}} \frac{\partial \mathbf{C}}{\partial \lambda} + \frac{\partial \Psi}{\partial \kappa} \frac{\partial \kappa}{\partial \lambda} + \sum_{\mu} \frac{\partial \Psi}{\partial \phi_{\mu}} \frac{\partial \phi_{\mu}}{\partial \lambda} \quad (33)$$

Often times, the basis set is independent of the perturbation (though not in the case of nuclear gradients since the basis functions are placed on the nuclei). Thus, we can write that

$$\left. \frac{\partial \mathcal{E}}{\partial \lambda} \right|_{\lambda=0} = \langle \Psi(0) | \hat{\mathbf{P}}_1 | \Psi(0) \rangle + 2 \frac{\partial \mathbf{C}}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial \mathbf{C}} \middle| \hat{H} \middle| \Psi(0) \right\rangle + 2 \frac{\partial \kappa}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial \kappa} \middle| \hat{H} \middle| \Psi(0) \right\rangle \quad (34)$$

Now, only for variational methods, where the final wave function is variationally optimized with respect to **all** parameters, the last two terms are zero since the energy is stationary with respect to the CI or MO coefficients! This is actually a variation of the more general **Hellmann-Feynman** theorem (see the next section).

$$\frac{\partial \mathcal{E}}{\partial \mathbf{C}} = 2 \left\langle \frac{d\Psi}{d\mathbf{C}} \middle| \hat{H} + \lambda \hat{\mathbf{P}}_1 + \lambda^2 \hat{\mathbf{P}}_2 \middle| \Psi \right\rangle = 0 \quad (35)$$

Thus, when $\lambda = 0$,

$$\left. \frac{\partial \mathcal{E}}{\partial \mathbf{C}} \right|_{\lambda=0} = 2 \left\langle \frac{\partial \Psi}{\partial \mathbf{C}} \middle| \hat{H} \middle| \Psi(0) \right\rangle = 0 \quad (36)$$

Therefore, the final derivative is given as (again, only for variational wave functions)

$$\left. \frac{\partial \mathcal{E}}{\partial \lambda} \right|_{\lambda=0} = \langle \Psi(0) | \hat{\mathbf{P}}_1 | \Psi(0) \rangle \quad (37)$$

2.1. Hellmann-Feynman Theorem.

Theorem 1 (Hellmann-Feynman). Suppose λ is some continuous parameter such that the Hamiltonian depends on it $\hat{H}(\lambda)$. Let $|\Psi(\lambda)\rangle$, $\mathcal{E}(\lambda)$ be a corresponding eigenstate and eigenvalue. Then

$$\frac{d\mathcal{E}}{d\lambda} = \langle \Psi(\lambda) | \frac{d\hat{H}}{d\lambda} | \Psi(\lambda) \rangle \quad (38)$$

There are various ways to prove this theorem, lets look at a more straightforward one:

Proof. Note that since $|\Psi(\lambda)\rangle$ is an eigenstate of $\hat{H}(\lambda)$ always, and for any value of λ , $\langle \Psi(\lambda) | \Psi(\lambda) \rangle = 1$, it follows that

$$\frac{d}{d\lambda} \langle \Psi(\lambda) | \Psi(\lambda) \rangle = 0 \quad (39)$$

Now, starting with the energy expression,

$$\begin{aligned} \frac{d\mathcal{E}}{d\lambda} &= \left\langle \frac{d\Psi}{d\lambda} \middle| \hat{H}(\lambda) \middle| \Psi(\lambda) \right\rangle + \left\langle \Psi(\lambda) \middle| \hat{H}(\lambda) \middle| \frac{d\Psi}{d\lambda} \right\rangle + \langle \Psi(\lambda) | \frac{d\hat{H}}{d\lambda} | \Psi(\lambda) \rangle \\ &= \mathcal{E}(\lambda) \left(\left\langle \frac{d\Psi}{d\lambda} \middle| \Psi(\lambda) \right\rangle + \left\langle \Psi(\lambda) \middle| \frac{d\Psi}{d\lambda} \right\rangle \right) + \langle \Psi(\lambda) | \frac{d\hat{H}}{d\lambda} | \Psi(\lambda) \rangle \\ &= \mathcal{E}(\lambda) \frac{d}{d\lambda} \langle \Psi(\lambda) | \Psi(\lambda) \rangle + \langle \Psi(\lambda) | \frac{d\hat{H}}{d\lambda} | \Psi(\lambda) \rangle \\ &= \langle \Psi(\lambda) | \frac{d\hat{H}}{d\lambda} | \Psi(\lambda) \rangle \end{aligned} \quad (40)$$

□

The Hellmann-Feynman theorem actually can be a bit looser in its requirements for $|\Psi(\lambda)\rangle$ which is that it is a stationary point of the energy. However, eigenstates are stationary points and thus eigenstates automatically satisfy this condition. Variational wave function are also stationary points of the energy with respect to the variational parameters, and thus also satisfy the condition. Non-variational wave functions **do not**, and hence one typically would have to compute the response of the wave function parameters to the external perturbation (which can be very costly).

2.2. Second Derivative of the Energy. The second derivative of the energy for a real-valued wave function can be written as

$$\begin{aligned} \frac{1}{2} \frac{\partial^2 \mathcal{E}}{\partial \lambda^2} &= \left\langle \frac{\partial^2 \Psi}{\partial \lambda^2} \left| \hat{H} + \lambda \hat{\mathbf{P}}_1 + \lambda^2 \hat{\mathbf{P}}_2 \right| \Psi \right\rangle + 2 \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \hat{\mathbf{P}}_1 + 2\lambda \hat{\mathbf{P}}_2 \right| \Psi \right\rangle \\ &+ \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \hat{H} + \lambda \hat{\mathbf{P}}_1 + \lambda^2 \hat{\mathbf{P}}_2 \right| \frac{\partial \Psi}{\partial \lambda} \right\rangle + \langle \Psi | \hat{\mathbf{P}} | \Psi \rangle \end{aligned} \quad (41)$$

Again, letting the perturbation strength go to zero,

$$\frac{1}{2} \frac{\partial^2 \mathcal{E}}{\partial \lambda^2} \Big|_{\lambda=0} = \left\langle \frac{\partial^2 \Psi}{\partial \lambda^2} \left| \hat{H} \right| \Psi(0) \right\rangle + 2 \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \hat{\mathbf{P}}_1 \right| \Psi(0) \right\rangle + \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \hat{H} \right| \frac{\partial \Psi}{\partial \lambda} \right\rangle + \langle \Psi(0) | \hat{\mathbf{P}}_2 | \Psi(0) \rangle \quad (42)$$

Now, lets suppose that only \mathbf{C} are our only variational parameters (they could encompass the MO coefficients as well, but we reduce it down to 1 symbol for simplicity), we can write the derivative as

$$\begin{aligned} \frac{1}{2} \frac{\partial^2 \mathcal{E}}{\partial \lambda^2} \Big|_{\lambda=0} &= \frac{\partial^2 \mathbf{C}}{\partial \lambda^2} \left\langle \frac{\partial \Psi}{\partial \mathbf{C}} \left| \hat{H} \right| \Psi(0) \right\rangle + \left(\frac{\partial \mathbf{C}}{\partial \lambda} \right)^2 \left\langle \frac{\partial^2 \Psi}{\partial \mathbf{C}^2} \left| \hat{H} \right| \Psi(0) \right\rangle \\ &+ 2 \frac{\partial \mathbf{C}}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial \mathbf{C}} \left| \hat{\mathbf{P}}_1 \right| \Psi(0) \right\rangle + \left(\frac{\partial \mathbf{C}}{\partial \lambda} \right)^2 \left\langle \frac{\partial \Psi}{\partial \mathbf{C}} \left| \hat{H} \right| \frac{\partial \Psi}{\partial \mathbf{C}} \right\rangle + \langle \Psi(0) | \hat{\mathbf{P}}_2 | \Psi(0) \rangle \end{aligned} \quad (43)$$

Again, assuming we have a variational wave function, we see that the first term is zero. The second, third, and fourth term sum to zero, which can be seen by calculating the second derivative of Eq. (36) with respect to the perturbation,

$$\begin{aligned} &\frac{\partial}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial \mathbf{C}} \left| \hat{H} + \lambda \hat{\mathbf{P}}_1 + \lambda^2 \hat{\mathbf{P}}_2 \right| \Psi(0) \right\rangle \Big|_{\lambda=0} \\ &= \frac{\partial \mathbf{C}}{\partial \lambda} \left\langle \frac{\partial^2 \Psi}{\partial \mathbf{C}^2} \left| \hat{H} \right| \Psi(0) \right\rangle + \left\langle \frac{\partial \Psi}{\partial \mathbf{C}} \left| \hat{\mathbf{P}}_1 \right| \Psi(0) \right\rangle + \frac{\partial \mathbf{C}}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial \mathbf{C}} \left| \hat{H} \right| \frac{\partial \Psi}{\partial \mathbf{C}} \right\rangle = 0 \end{aligned} \quad (44)$$

All of this allows us to simplify the second derivative to (again, only for variational methods)

$$\frac{1}{2} \frac{\partial^2 \mathcal{E}}{\partial \lambda^2} \Big|_{\lambda=0} = \langle \Psi(0) | \hat{\mathbf{P}}_2 | \Psi(0) \rangle + \frac{\partial \mathbf{C}}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial \mathbf{C}} \left| \hat{\mathbf{P}}_1 \right| \Psi(0) \right\rangle \quad (45)$$

or, written more compactly as

$$\frac{1}{2} \frac{\partial^2 \mathcal{E}}{\partial \lambda^2} \Big|_{\lambda=0} = \langle \Psi(0) | \hat{\mathbf{P}}_2 | \Psi(0) \rangle + \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \hat{\mathbf{P}}_1 \right| \Psi(0) \right\rangle \quad (46)$$

What is evident is that even for variational methods, if we want the second derivative of the energy, we must compute the response of the wave function! This is why quantities such as Hessians are much more expensive to compute as compared to gradients.

2.3. Derivative Methods versus Perturbation Theory. Only for exact wave functions do first or second order perturbation theory give identical quantities to the derivative methods. In general though, they are different it has been shown that these differences can be quite significant. It is therefore favored (when ever possible) to compute these properties using the derivative methods as they will give the correct value irregardless of if the method is variational or not.