

DIPOLE MOMENT AND NUCLEAR GRADIENTS

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1. PERMANENT DIPOLE MOMENTS

From before, we know that the permanent dipole moment is given by the first derivative of the energy with respect to an external electric field, evaluated with zero field.

$$\boldsymbol{\mu}_0 = - \left. \frac{\partial \mathcal{E}}{\partial \mathbf{E}} \right|_{\mathbf{E}=0} \quad (1)$$

The energy in the presence of an external electric field is given by

$$\mathcal{E}(\mathbf{E}) = \mathcal{E}(0) - \langle \Psi | \hat{\boldsymbol{\mu}} | \Psi \rangle \cdot \mathbf{E} + \mathcal{O}(\mathbf{E}^2) \quad (2)$$

Here, we define the full dipole moment operator $\hat{\boldsymbol{\mu}}$ as

$$\hat{\boldsymbol{\mu}} = -\hat{\mathbf{r}} + \sum_A Z_A \mathbf{R}_A \quad (3)$$

where Z_A is the charge of the A th nuclei. Note that within the Born-Oppenheimer approximation, \mathbf{R}_A , which are the nuclear positions, are not promoted to operators, and that term is evaluated as a constant (similar to the nuclear-nuclear repulsion term). Given the energy expression above, we can write that our Hamiltonian (in the presence of an external electric field) is given as

$$\hat{H}(\mathbf{E}) = \hat{H}(0) - \hat{\boldsymbol{\mu}} \cdot \mathbf{E} + \mathcal{O}(\mathbf{E}^2) \quad (4)$$

Lets see how we can evaluate the dipole moment for both HF and truncated CI, illustrating the differences between the variational and non-variational methods.

1.1. Hartree-Fock Dipole Moments. Since the Hartree-Fock wave function is fully variational, we can use the Hellmann-Feynman theorem to simply evaluate the permanent dipole moment. Hence, using ??, we have that $\hat{\mathbf{P}}_1 = -\hat{\boldsymbol{\mu}}$ and therefore,

$$\boldsymbol{\mu}_0 = \langle \Psi(0) | \hat{\boldsymbol{\mu}} | \Psi(0) \rangle \quad (5)$$

where $|\Psi(0)\rangle$ is the Hartree-Fock ground state wave function. We can of course express this in terms of the AO integrals and AO density matrix elements as

$$\begin{aligned} \boldsymbol{\mu}_0 &= - \langle \Psi(0) | \hat{\mathbf{r}} | \Psi(0) \rangle + \sum_A Z_A \mathbf{R}_A \\ &= - \sum_{\mu\nu} D_{\mu\nu} \mathbf{r}_{\mu\nu} + \sum_A Z_A \mathbf{R}_A \end{aligned} \quad (6)$$

where

$$\mathbf{r}_{\mu\nu} = \langle \phi_\mu | \hat{\mathbf{r}} | \phi_\nu \rangle \quad (7)$$

are just integrals over the spatial operator. These integrals are readily available in various integral solver packages.

1.2. **Truncated CI.** Lets suppose that we have now a wave function $|\Psi\rangle$ from some truncated CI calculation. For concreteness, suppose it is CISD. Now, $|\Psi\rangle$ is not fully variational since the orbitals have come from a HF calculation, whereas the CI coefficients were variationally optimized. Another way of putting it is that when we start to change the CI coefficients, the HF orbitals may not longer represent stationary points. Let \mathbf{C} be the CI coefficient parameters and $\boldsymbol{\kappa}$ to MO coefficients. Now,

$$\frac{\partial \mathcal{E}^{\text{CISD}}}{\partial \boldsymbol{\kappa}} \neq 0 \quad (8)$$

but

$$\frac{\partial \mathcal{E}^{\text{HF}}}{\partial \boldsymbol{\kappa}} = 0 \quad (9)$$

Furthermore,

$$\frac{\partial \mathcal{E}^{\text{CISD}}}{\partial \mathbf{C}} = 0 \quad (10)$$

Now, because our energy is not fully-variational, we will need to calculate the response of the wave function to the electric field. However, we can avoid this by using Lagranges method of undetermined multipliers. We construct our Lagrangian as

$$\mathcal{L} = \mathcal{E}^{\text{CISD}} + \bar{\boldsymbol{\kappa}} \cdot \frac{\partial \mathcal{E}^{\text{HF}}}{\partial \boldsymbol{\kappa}} \quad (11)$$

where $\bar{\boldsymbol{\kappa}}$ is our multiplier that we determine such that \mathcal{L} is fully variational with respect to both \mathbf{C} , $\bar{\boldsymbol{\kappa}}$, and $\boldsymbol{\kappa}$. Note that \mathcal{L} is already stationary with respect to \mathbf{C} and $\bar{\boldsymbol{\kappa}}$, so we only have to make it stationary with respect to $\boldsymbol{\kappa}$. If we begin, we see that

$$\frac{\partial \mathcal{L}}{\partial \boldsymbol{\kappa}} = \frac{\partial \mathcal{E}^{\text{CISD}}}{\partial \boldsymbol{\kappa}} + \bar{\boldsymbol{\kappa}} \cdot \frac{\partial^2 \mathcal{E}^{\text{HF}}}{\partial \boldsymbol{\kappa}^2} = 0 \quad (12)$$

Firstly, $\frac{\partial^2 \mathcal{E}^{\text{HF}}}{\partial \boldsymbol{\kappa}^2}$ is the Hessian of the HF energy with respect to MO parameters, which we label as $\mathbf{H}_{\boldsymbol{\kappa}}^{\text{HF}}$. We can therefore solve for $\bar{\boldsymbol{\kappa}}$ by solving the following coupled linear equations

$$\frac{\partial \mathcal{E}^{\text{CISD}}}{\partial \boldsymbol{\kappa}} = -\mathbf{H}_{\boldsymbol{\kappa}}^{\text{HF}} \cdot \bar{\boldsymbol{\kappa}} \quad (13)$$

In general, $\mathbf{H}_{\boldsymbol{\kappa}}^{\text{HF}}$ is too large to invert, and so various algorithms exist to solve this set of coupled equations. Additionally, if there are any redundancies with respect to the orbital coefficients, this can cause singularities in the Hessian and make the equation undefined. Therefore, it is imperative to remove any redundancies prior to solving.

Having solved for $\bar{\boldsymbol{\kappa}}$, the dipole moment can be calculated by

$$\boldsymbol{\mu}_0 = - \left. \frac{\partial \mathcal{L}}{\partial \mathbf{E}} \right|_{\mathbf{E}=0} \quad (14)$$

and using the Hellmann-Feynman theorem. This is valid since \mathcal{L} is stationary with respect to all variational parameters! We did not include the electric field explicitly in the

construction of the Lagrangian, as in all steps that we care about, the field is evaluated at 0. Hence, it only formally shows up here at the end. That is

$$\mathcal{E}^{\text{CISD}} = \langle \Psi | \hat{H} - \hat{\boldsymbol{\mu}} \cdot \mathbf{E} | \Psi \rangle \quad (15)$$

and

$$\mathcal{E}^{\text{HF}} = \langle \text{HF} | \hat{H} - \hat{\boldsymbol{\mu}} \cdot \mathbf{E} | \text{HF} \rangle \quad (16)$$

Thus,

$$\boldsymbol{\mu}_0 = \langle \Psi | \hat{\boldsymbol{\mu}} | \Psi \rangle + \bar{\kappa} \frac{\partial}{\partial \boldsymbol{\kappa}} \langle \text{HF} | \hat{\boldsymbol{\mu}} | \text{HF} \rangle \quad (17)$$

The first term is the **unrelaxed** CISD dipole moment. That is, it is the first-order perturbation theory dipole moment for CISD. Note that it is called the unrelaxed dipole moment since it does not take into account fully the electron correlation. The second term, with the Lagrange multipliers, gives a correction from this dipole moment such that the entire dipole moment is called the **relaxed** CISD dipole moment.

I do admit that the equations above are not fully implementable as there are some details which are left out. Specifically, how does one take derivatives with respect to orbital coefficients. This unfortunately, leads to all sort of issues with redundant parameters and how one actually expresses the parameterization of the wave function which is beyond the scope of this course. Instead, just know that the second term involves the HF RDM elements and is relatively straightforward to compute.

The hardest step, of all, is the calculation of the Lagrange multipliers; and often, quantum chemistry software packages will only report the unrelaxed CISD dipole moment. There might be explicit keywords that can instead return the more correct/accurate relaxed dipole moment, but this is up to the individual software packages.

2. NUCLEAR GRADIENTS

Now we turn to something that we use routinely, and for which, it is very important to get correct. Incorrect nuclear gradients are ultimately not useful at all since they will lead to wrong geometries during geometry optimizations, and fail to accurately evolve along the potential energy surface during *ab initio* molecular dynamics. First, we will consider the Hartree-Fock gradients and then consider how one would compute nuclear gradients for a non-variational method.

Generally speaking, the nuclear gradient is given by

$$\frac{\partial \mathcal{E}}{\partial \mathbf{R}} = \langle \Psi | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi \rangle + 2 \left\langle \frac{\partial \Psi}{\partial \mathbf{R}} \left| \hat{H} \right| \Psi \right\rangle \quad (18)$$

Unlike in the dipole moment, the second term is not zero. This is because the orbitals depend on the nuclear coordinates as they are centered on them. That is, if the nuclei are moved an infinitesimal amount, the basis set has also changed and we must account for this. However, if we were using a plane-wave basis (for a periodic calculation), then the gradient would just be the normal Hellmann-Feynman term.

2.1. Analytic Hartree-Fock Nuclear Gradients. Lets start with considering the restricted, closed shell Hartree-Fock energy in terms of the AO basis functions as

$$\mathcal{E} = \sum_{\mu\nu} D_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\tau\sigma} D_{\mu\nu} D_{\tau\sigma} (g_{\mu\nu\tau\sigma} - g_{\mu\sigma\tau\nu}) + V^{\text{nuc}} \quad (19)$$

If one now takes the derivative with respect to some geometrical displacement (call it λ), then

$$\begin{aligned} \frac{\partial \mathcal{E}}{\partial \lambda} &= \sum_{\mu\nu} \left(\frac{\partial D_{\mu\nu}}{\partial \lambda} h_{\mu\nu} + D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial \lambda} \right) \\ &+ \frac{1}{2} \sum_{\mu\nu\tau\sigma} \left(\frac{\partial D_{\mu\nu}}{\partial \lambda} D_{\tau\sigma} + D_{\mu\nu} \frac{\partial D_{\tau\sigma}}{\partial \lambda} \right) (g_{\mu\nu\tau\sigma} - g_{\mu\sigma\tau\nu}) \\ &+ \frac{1}{2} \sum_{\mu\nu\tau\sigma} D_{\mu\nu} D_{\tau\sigma} \frac{\partial}{\partial \lambda} (g_{\mu\nu\tau\sigma} - g_{\mu\sigma\tau\nu}) + \frac{\partial V^{\text{nuc}}}{\partial \lambda} \end{aligned} \quad (20)$$

The third and fourth term can be collected since they are identical, removing the factor of 1/2. Lets rearrange this a bit

$$\begin{aligned} \frac{\partial \mathcal{E}}{\partial \lambda} &= \sum_{\mu\nu} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial \lambda} + \frac{1}{2} \sum_{\mu\nu\tau\sigma} D_{\mu\nu} D_{\tau\sigma} \frac{\partial}{\partial \lambda} (g_{\mu\nu\tau\sigma} - g_{\mu\sigma\tau\nu}) \\ &+ \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial \lambda} h_{\mu\nu} + \sum_{\mu\nu\tau\sigma} \frac{\partial D_{\mu\nu}}{\partial \lambda} D_{\tau\sigma} (g_{\mu\nu\tau\sigma} - g_{\mu\sigma\tau\nu}) + \frac{\partial V^{\text{nuc}}}{\partial \lambda} \end{aligned} \quad (21)$$

The first two terms involve the derivative of the atomic integrals while the next two terms involve derivatives of the density matrix times the Fock matrix! So we can simplify these quantities as

$$\sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial \lambda} F_{\mu\nu} \quad (22)$$

The derivative of the nuclear repulsion term is trivial since it doesn't involve any electron coordinates (it can be done analytically very simply).

Lets now consider the derivatives of the integrals. The one-electron derivatives are given as

$$\frac{\partial h_{\mu\nu}}{\partial \lambda} = \left\langle \frac{\partial \phi_\mu}{\partial \lambda} \left| \hat{h} \right| \phi_\nu \right\rangle + \left\langle \phi_\mu \left| \frac{\partial \hat{h}}{\partial \lambda} \right| \phi_\nu \right\rangle + \left\langle \phi_\mu \left| \hat{h} \right| \frac{\partial \phi_\nu}{\partial \lambda} \right\rangle \quad (23)$$

All three terms will be necessary since the core operator depends on the nuclei for the nuclear-electron repulsion term. For the two-electron derivatives we have

$$\begin{aligned} \frac{\partial g_{\mu\nu\tau\sigma}}{\partial \lambda} &= \left\langle \frac{\partial \phi_\mu}{\partial \lambda} \phi_\tau \left| \hat{g} \right| \phi_\nu \phi_\sigma \right\rangle + \left\langle \phi_\mu \frac{\partial \phi_\tau}{\partial \lambda} \left| \hat{g} \right| \phi_\nu \phi_\sigma \right\rangle \\ &+ \left\langle \phi_\mu \phi_\tau \left| \hat{g} \right| \frac{\partial \phi_\nu}{\partial \lambda} \phi_\sigma \right\rangle + \left\langle \phi_\mu \phi_\tau \left| \hat{g} \right| \phi_\nu \frac{\partial \phi_\sigma}{\partial \lambda} \right\rangle \end{aligned} \quad (24)$$

Notice that there is no Hellmann-Feynman term for the two-electron integral since the electron-repulsion operator does not depend on the nuclei at all. All of these integrals can be readily evaluated using various techniques. This is especially true for Gaussian orbitals, as the derivative with respect to the nuclear position will return a Gaussian with just different angular components.

Finally, let's deal with the derivatives of the density matrix. Recall that the density matrix is built from the MO coefficients as

$$D_{\mu\nu} = 2 \sum_i^{N/2} C_{\mu i} C_{\nu i} \quad (25)$$

where the summation i is only over the double occupied orbitals (inactive). Then, if we propagate the derivative, we have that

$$\frac{\partial D_{\mu\nu}}{\partial \lambda} = 2 \sum_i^{N/2} \left(\frac{\partial C_{\mu i}}{\partial \lambda} C_{\nu i} + C_{\mu i} \frac{\partial C_{\nu i}}{\partial \lambda} \right) \quad (26)$$

Therefore, we can write that

$$\sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial \lambda} F_{\mu\nu} = 2 \sum_{\mu\nu} \sum_i^{N/2} \left(\frac{\partial C_{\mu i}}{\partial \lambda} F_{\mu\nu} C_{\nu i} + \frac{\partial C_{\nu i}}{\partial \lambda} F_{\mu\nu} C_{\mu i} \right) \quad (27)$$

But now, recall that $C_{\mu i}$ are determined through the HF condition

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad (28)$$

Substitution therefore leads to

$$\sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial \lambda} F_{\mu\nu} = 2 \sum_{\mu\nu} \sum_i^{N/2} \left(\frac{\partial C_{\mu i}}{\partial \lambda} S_{\mu\nu} \varepsilon_i C_{\nu i} + \frac{\partial C_{\nu i}}{\partial \lambda} S_{\mu\nu} \varepsilon_i C_{\mu i} \right) \quad (29)$$

Finally, we will deal with the derivatives of the MO coefficients by replacing them with derivatives of the overlap matrix. We start by noting that the MOs are orthonormal such that

$$\langle \phi_i | \phi_j \rangle = \sum_{\mu\nu} C_{\mu i} C_{\nu j} \langle \phi_\mu | \phi_\nu \rangle = \sum_{\mu\nu} C_{\mu i} C_{\nu j} S_{\mu\nu} = \delta_{ij} \quad (30)$$

This must hold for *any* geometry λ . Hence, the derivative must be zero such that we can write

$$\frac{\partial \langle \phi_i | \phi_j \rangle}{\partial \lambda} = \sum_{\mu\nu} \left(\frac{\partial C_{\mu i}}{\partial \lambda} C_{\nu j} S_{\mu\nu} + C_{\mu i} \frac{\partial C_{\nu j}}{\partial \lambda} S_{\mu\nu} + C_{\mu i} C_{\nu j} \frac{\partial S_{\mu\nu}}{\partial \lambda} \right) = 0 \quad (31)$$

Rearranging leads to the following identity,

$$2 \sum_{\mu\nu} \frac{\partial C_{\mu i}}{\partial \lambda} C_{\nu j} S_{\mu\nu} = - \sum_{\mu\nu} C_{\mu i} C_{\nu j} \frac{\partial S_{\mu\nu}}{\partial \lambda} \quad (32)$$

We can use this identity to replace the density matrix derivatives with derivatives of the overlap matrix. In total, we find that the final derivative of the Hartree-Fock energy is

$$\begin{aligned} \frac{\partial \mathcal{E}}{\partial \lambda} &= \sum_{\mu\nu} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial \lambda} + \frac{1}{2} \sum_{\mu\nu\tau\sigma} D_{\mu\nu} D_{\tau\sigma} \frac{\partial}{\partial \lambda} (g_{\mu\nu\tau\sigma} - g_{\mu\sigma\tau\nu}) \\ &+ \frac{\partial V^{\text{nuc}}}{\partial \lambda} - \sum_{\mu\nu} \sum_i^{N/2} C_{\mu i} C_{\nu i} \varepsilon_i \frac{\partial S_{\mu\nu}}{\partial \lambda} \end{aligned} \quad (33)$$

In the literature, the final term is often called the **renormalization** or **connection term** and quite frankly, is never well explained. Here, in first quantization, it is quite evident where this term comes from: moving the nuclei moves the AO's and thus the MO coefficients depend on this. An alternative formulation would be to construct a Lagrangian with the Hartree-Fock energy plus a constraint that the orbitals are orthonormal at all geometries. The corresponding Lagrange multipliers would exactly recover this renormalization term. Similar terms appear in MC-SCF, CI, etc nuclear gradients, though they are often computed using what is called the **generalized Fock matrix**.

2.2. Non-variational Nuclear Gradients. Lets now consider how to compute the nuclear gradients for a method which is not fully variational with respect to all wave function parameters. Similar to what we did in the dipole moment case, we will also form a Lagrangian and make it variational with respect to these wave function parameters, but omit the basis set. We can deal with the basis set dependence explicitly, just like we did in the HF case. If we take CISD as our example, the MO coefficients come from making the HF energy stationary; hence, we will use the same Lagrangian as in the CISD dipole moment (Eq. (11)).

$$\mathcal{L} = \mathcal{E}^{\text{CISD}} + \bar{\kappa} \cdot \frac{\partial \mathcal{E}^{\text{HF}}}{\partial \kappa} \quad (34)$$

Again, we will know how to solve for the Lagrange multiplier $\bar{\kappa}$ which comes from making \mathcal{L} stationary with respect to κ . Then, we can take the derivative with respect to our nuclear coordinate λ as

$$\frac{\partial \mathcal{L}}{\partial \lambda} = \frac{\partial \mathcal{E}^{\text{CISD}}}{\partial \lambda} + \bar{\kappa} \cdot \frac{\partial}{\partial \kappa} \frac{\partial \mathcal{E}^{\text{HF}}}{\partial \lambda} \quad (35)$$

We already know how to take the derivative $\frac{\partial \mathcal{E}^{\text{HF}}}{\partial \lambda}$, and one can then take a derivative with respect to the MO coefficients. The first term, which is the derivative of the CISD energy with respect to the nuclear displacement, will be evaluated similarly to the HF energy. There will be an explicit contribution which contains the derivative integrals, and then a renormalization term. It is beyond the scope of this text/class to write down what these equations are explicitly, especially given they are much more concise/easier to derive in the second-quantization formalism.

3. WAVE FUNCTION RESPONSE AND SECOND-ORDER DERIVATIVES

Lets suppose that we wanted to calculate the nuclear hessian analytically. This will require the response of the wave function to the external perturbation (nuclear coordinate in this case) and therefore will require a lot more work. Lets consider it here for the HF case.

3.1. **Hartree-Fock Nuclear Hessian.** One can just take another derivative of the HF energy with respect to some nuclear coordinate λ_2

$$\begin{aligned}
\frac{\partial^2 \mathcal{E}^{\text{HF}}}{\partial \lambda_1 \partial \lambda_2} &= \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial \lambda_1 \partial \lambda_2} + \frac{1}{2} \sum_{\mu\nu\tau\sigma} D_{\mu\nu} D_{\tau\sigma} \frac{\partial^2}{\partial \lambda_1 \partial \lambda_2} (g_{\mu\nu\tau\sigma} - g_{\mu\sigma\tau\nu}) \\
&+ \frac{\partial^2 V^{\text{nuc}}}{\partial \lambda_1 \partial \lambda_2} - \sum_{\mu\nu} \sum_i^{N/2} C_{\mu i} C_{\nu i} \varepsilon_i \frac{\partial^2 S_{\mu\nu}}{\partial \lambda_1 \partial \lambda_2} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial \lambda_2} \frac{\partial h_{\mu\nu}}{\partial \lambda_1} \\
&+ \sum_{\mu\nu\tau\sigma} \frac{\partial D_{\mu\nu}}{\partial \lambda_2} D_{\tau\sigma} \frac{\partial}{\partial \lambda_1} (g_{\mu\nu\tau\sigma} - g_{\mu\sigma\tau\nu}) \\
&- \sum_{\mu\nu} \frac{\partial}{\partial \lambda_2} \left(\sum_i^{N/2} C_{\mu i} C_{\nu i} \varepsilon_i \right) \frac{\partial S_{\mu\nu}}{\partial \lambda_1}
\end{aligned} \tag{36}$$

We can evaluate the first 4 terms, as they correspond to derivatives of integrals. The last 3 terms involve derivatives of the wave function (density matrix and MO energies). We can obtain these values by solving the first-order coupled-perturbed Hartree-Fock equations.