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Introduction to the calculation of molecular properties by response theory

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This document reviews the calculation of time-independent and time-dependent molecular properties in quantum chemistry. Sections 1.1, 1.2 and 1.3 are inspired to a large extent by the lectures of Prof. Trygve Helgaker (University of Oslo, Norway) [1]. For more intensive reviews, see Refs. [2–4].

1 Time-independent molecular properties

1.1 Definition

We consider an isolated molecular system of Hamiltonian \hat{H}_0 , and apply a static perturbation $\hat{V}(x)$, depending on a variable x (representing the strength of the perturbation), such that the perturbation vanishes for $x = 0$. The perturbed Hamiltonian is

$$\hat{H}(x) = \hat{H}_0 + \hat{V}(x), \quad (1)$$

and the total energy can be expanded with respect to x as

$$\mathcal{E}(x) = \frac{\langle \Psi(x) | \hat{H}(x) | \Psi(x) \rangle}{\langle \Psi(x) | \Psi(x) \rangle} = \mathcal{E}^{(0)} + \mathcal{E}^{(1)}x + \frac{1}{2}\mathcal{E}^{(2)}x^2 + \dots, \quad (2)$$

where $\Psi(x)$ is the wave function of the state considered, which is usually the ground state. In this expansion, $\mathcal{E}^{(0)} = \mathcal{E}_0$ is the unperturbed energy associated to the Hamiltonian \hat{H}_0 , and the energy derivatives

$$\mathcal{E}^{(1)} = \left. \frac{d\mathcal{E}}{dx} \right|_{x=0}; \quad \mathcal{E}^{(2)} = \left. \frac{d^2\mathcal{E}}{dx^2} \right|_{x=0}; \quad \text{etc...} \quad (3)$$

are called *time-independent molecular properties*. They are characteristic of the molecule and its quantum state, and contain important information about the response of the system to the perturbation.

1.2 Examples

1.2.1 Geometrical derivatives

One the most important example of a static perturbation is a deformation of the molecular geometry (in the Born-Oppenheimer approximation). In this case, x corresponds to variations of nuclei positions ΔR_i , and the total energy is expanded as

$$\mathcal{E}(\{R_i\}) = \mathcal{E}^{(0)} + \sum_i \mathcal{E}_i^{(1)} \Delta R_i + \frac{1}{2} \sum_{i,j} \mathcal{E}_{i,j}^{(2)} \Delta R_i \Delta R_j + \dots, \quad (4)$$

where

$$\mathcal{E}_i^{(1)} = \frac{\partial \mathcal{E}}{\partial R_i} \quad (5)$$

is called the *molecular gradient*, and

$$\mathcal{E}_{i,j}^{(2)} = \frac{\partial^2 \mathcal{E}}{\partial R_i \partial R_j} \quad (6)$$

is called the *molecular Hessian*. These quantities are used in geometry optimization for locating and characterizing critical points on the molecular potential energy surface (energy minimum, saddle point at a transition state). There are also used for calculating spectroscopic constants such as harmonic vibrational frequencies. Note that anharmonicity vibrational corrections require the calculation of third-order derivatives $\mathcal{E}_{i,j,k}^{(3)} = \partial^3 \mathcal{E} / \partial R_i \partial R_j \partial R_k$.

1.2.2 Electric properties

In this case, the perturbation applied is an external electrostatic potential $v(\mathbf{r})$. Let us consider the corresponding interaction energy

$$\mathcal{E}_{\text{int}} = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r}, \quad (7)$$

where $n(\mathbf{r})$ is the charge density of the system. Expanding the potential $v(\mathbf{r})$ around an origin point $\mathbf{r} = \mathbf{0}$, we have

$$\begin{aligned} v(\mathbf{r}) &= v(\mathbf{0}) + \sum_i \left. \frac{\partial v}{\partial r_i} \right|_{\mathbf{r}=\mathbf{0}} r_i + \frac{1}{2} \sum_{i,j} \left. \frac{\partial^2 v}{\partial r_i \partial r_j} \right|_{\mathbf{r}=\mathbf{0}} r_i r_j + \dots \\ &= v(\mathbf{0}) - \sum_i E_i r_i - \frac{1}{2} \sum_{i,j} F_{i,j} r_i r_j + \dots, \end{aligned} \quad (8)$$

where $v(\mathbf{0})$ is a constant potential, E_i are the components of the corresponding electric field, and $F_{i,j}$ are the components of the electric field gradient. The interaction energy can thus be expanded as

$$\mathcal{E}_{\text{int}} = q v(\mathbf{0}) - \sum_i \mu_i E_i - \frac{1}{2} \sum_{i,j} Q_{i,j} F_{i,j} + \dots, \quad (9)$$

where $q = \int n(\mathbf{r})d\mathbf{r}$ is the *electric charge* of the system, $\mu_i = \int n(\mathbf{r})r_i d\mathbf{r}$ are the components of the *electric dipole moment*, and $Q_{i,j} = \int n(\mathbf{r})r_i r_j d\mathbf{r}$ are the components of *electric quadrupole moment*. Hence, these properties can be defined as energy derivatives

$$q = \frac{\partial \mathcal{E}}{\partial v(\mathbf{0})}; \quad \mu_i = -\frac{\partial \mathcal{E}}{\partial E_i}; \quad Q_{i,j} = -2\frac{\partial \mathcal{E}}{\partial F_{i,j}}. \quad (10)$$

We can further decompose the dipole moment into permanent and field-induced contributions

$$\mu_i = \mu_{0,i} + \sum_j \alpha_{i,j} E_j + \dots, \quad (11)$$

which leads to the definition of the *permanent electric dipole moment*

$$\mu_{0,i} = -\left. \frac{\partial \mathcal{E}}{\partial E_i} \right|_{\mathbf{E}=\mathbf{0}}, \quad (12)$$

and the *electric dipole polarizability*

$$\alpha_{i,j} = -\left. \frac{\partial^2 \mathcal{E}}{\partial E_i \partial E_j} \right|_{\mathbf{E}=\mathbf{0}}. \quad (13)$$

1.2.3 Magnetic properties

For magnetic properties, we consider the double expansion of the total energy with respect to nuclear magnetic dipole moments m_a (a refers to an atomic nucleus) and an externally applied magnetic field B

$$\mathcal{E}(\{m_a\}, B) = \mathcal{E}^{(0)} + \sum_a \mathcal{E}_a^{(10)} m_a + \mathcal{E}^{(01)} B + \frac{1}{2} \sum_{a,b} \mathcal{E}_{a,b}^{(20)} m_a m_b + \sum_a \mathcal{E}_a^{(11)} m_a B + \frac{1}{2} \mathcal{E}^{(02)} B^2 + \dots, \quad (14)$$

the dependence of the total energy on the nuclear magnetic dipole moments requiring the inclusion of the hyperfine-interaction terms in the Hamiltonian.

In nuclear magnetic resonance (NMR), we measure the coupling between m_a and B , which is quantified by the second-order derivative

$$\mathcal{E}_a^{(11)} = \frac{\partial^2 \mathcal{E}}{\partial m_a \partial B}. \quad (15)$$

In vacuum, the interaction energy is simply $\mathcal{E}_{\text{vac}} = -m_a B$, giving $\mathcal{E}_{a,\text{vac}}^{(11)} = -1$. In a molecule, due to the presence of electrons, it is modified by a few ppm, and we write $\mathcal{E}_{a,\text{mol}}^{(11)} = -1 + \sigma_a$ where σ_a is the *NMR shielding constant* of the nucleus a . We also measure the nuclear spin-spin coupling constants between two nuclei

$$\mathcal{E}_{a,b}^{(20)} = \frac{\partial^2 \mathcal{E}}{\partial m_a \partial m_b} = J_{a,b}. \quad (16)$$

In solution, only the indirect contribution to this coupling (mediated by the electrons) survives and provides useful geometrical information about the molecule.

Similarly to the corresponding electric properties, we can also define properties such as the *permanent magnetic dipole moment* $M_0 = -\partial \mathcal{E} / \partial B|_{B=0}$ and the *dipole magnetizability* $\xi = -\partial^2 \mathcal{E} / \partial B^2|_{B=0}$.

There are also other important magnetic properties used in electron paramagnetic resonance (EPR) such as *EPR hyperfine coupling constants* and *g values*.

1.3 Calculation of energy derivatives

1.3.1 Numerical versus analytical differentiation

There are two ways of calculating derivatives, by *numerical differentiation* and by *analytical differentiation*.

In numerical differentiation, the derivatives are calculated by finite differences or by polynomial fitting.

- It is simple to implement.
- The numerical precision is limited.
- The computational efficiency is low.
- It is not general. Usually, only real-valued and static perturbations can be done.

In analytical differentiation, the derivatives are calculated explicitly from the analytical expressions.

- It is difficult to implement.
- The precision is higher.
- The computational efficiency is higher.
- It is more general. In particular, frequency-dependent perturbations are possible.

Overall, analytical differentiation is preferable.

1.3.2 Sum-over-state expression for exact wave functions

For “exact” wave functions (full configuration interaction in a basis), we can use straightforward perturbation theory to find the expression of the energy derivatives. Expanding the perturbation operator $\hat{V}(x)$ in powers of x , we have

$$\hat{H}(x) = \hat{H}_0 + \hat{V}^{(1)}x + \frac{1}{2}\hat{V}^{(2)}x^2 + \dots . \quad (17)$$

The first-order energy derivative is

$$\mathcal{E}^{(1)} = \langle \Psi_0 | \hat{V}^{(1)} | \Psi_0 \rangle, \quad (18)$$

where Ψ_0 is the exact wave function of the unperturbed Hamiltonian \hat{H}_0 for the state considered, normalized such that $\langle \Psi_0 | \Psi_0 \rangle = 1$. Similarly, the second-order energy derivative is found from the first-order wave function correction $\Psi^{(1)}$, using intermediate normalization $\langle \Psi_0 | \Psi(x) \rangle = 1$,

$$\begin{aligned} \mathcal{E}^{(2)} &= \langle \Psi_0 | \hat{V}^{(2)} | \Psi_0 \rangle + 2\langle \Psi_0 | \hat{V}^{(1)} | \Psi^{(1)} \rangle \\ &= \langle \Psi_0 | \hat{V}^{(2)} | \Psi_0 \rangle - 2 \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{V}^{(1)} | \Psi_n \rangle \langle \Psi_n | \hat{V}^{(1)} | \Psi_0 \rangle}{\mathcal{E}_n - \mathcal{E}_0}, \end{aligned} \quad (19)$$

where Ψ_n and \mathcal{E}_n form a set of complete exact eigenstates and associated eigenvalues of \hat{H}_0 .

This last expression is very impractical since we need to know all the exact states of \hat{H}_0 , which is a complicated many-body Hamiltonian. Moreover, for approximate methods such as Hartree-Fock, it is not clear what we should use for Ψ_n and \mathcal{E}_n .

1.3.3 General expressions for approximate methods

In an (approximate) electronic-structure method, the total energy $\mathcal{E}(x)$ is obtained by optimizing parameters $\mathbf{p} = (p_1, p_2, \dots)$ in an energy function $E(x, \mathbf{p})$ for each fixed value of x . The final total energy $\mathcal{E}(x)$ is obtained for the optimal value of the parameters $\mathbf{p}^o(x)$ which are functions of x

$$\mathcal{E}(x) = E(x, \mathbf{p}^o(x)). \quad (20)$$

Note that the optimization is not necessarily variational, i.e. the optimization criterion is not necessarily to minimize $E(x, \mathbf{p})$ with respect to the parameters \mathbf{p} .

Examples:

- Hartree-Fock (HF), Kohn-Sham (KS): \mathbf{p} are the orbital parameters. The parameters are variational.
- Multiconfiguration self-consistent field (MCSCF): \mathbf{p} are the coefficients of the configurations (or determinants) and the orbital parameters. All parameters are variational.
- Configuration interaction (CI): \mathbf{p} are the coefficients of the configurations (or determinants) and the orbital parameters. The coefficients of the configurations are variational but not the orbital parameters.
- Coupled cluster (CC): \mathbf{p} are the cluster amplitudes and the orbital parameters. None parameters are variational.

First-order energy derivative

The first-order derivative of $\mathcal{E}(x)$ with respect to x is made of two terms

$$\frac{d\mathcal{E}(x)}{dx} = \frac{\partial E(x, \mathbf{p}^\circ)}{\partial x} + \sum_i \left. \frac{\partial E(x, \mathbf{p})}{\partial p_i} \right|_{\mathbf{p}=\mathbf{p}^\circ} \frac{\partial p_i^\circ}{\partial x}, \quad (21)$$

where the first term constitutes the *explicit dependence on x* and the second term constitutes the *implicit dependence on x* . The derivative $\partial p_i^\circ / \partial x$ appearing in the second term is called the *wave-function linear-response vector* and contains information about how the electronic structure changes when the system is perturbed. It is not straightforward to calculate it since we do not know explicitly dependence of p_i° on x .

Where all the parameters are variational, there is an important simplification. Indeed, in this case, the stationary condition (zero electronic gradient)

$$\left. \frac{\partial E(x, \mathbf{p})}{\partial p_i} \right|_{\mathbf{p}=\mathbf{p}^\circ} = 0, \quad (22)$$

implies that the second term in Eq. (21) vanishes, so the first-order energy derivative reduces to

$$\frac{d\mathcal{E}(x)}{dx} = \frac{\partial E(x, \mathbf{p}^\circ)}{\partial x}, \quad (23)$$

and we do not need the wave-function linear-response vector.

For example, for the calculation of the HF molecular gradient, we need to consider only the explicit dependence on the nuclear positions in the Hamiltonian and in the wave function, but not the implicit dependence of the orbital coefficients on the nuclear positions since these parameters are variational.

Second-order energy derivative

We will only consider the case where all the parameters are variational. In this case, the second-order derivative of $\mathcal{E}(x)$ is obtained by taking the derivative of Eq. (23)

$$\frac{d^2\mathcal{E}(x)}{dx^2} = \frac{\partial^2 E(x, \mathbf{p}^\circ)}{\partial x^2} + \sum_i \left. \frac{\partial^2 E(x, \mathbf{p})}{\partial x \partial p_i} \right|_{\mathbf{p}=\mathbf{p}^\circ} \frac{\partial p_i^\circ}{\partial x}, \quad (24)$$

where the *perturbed electronic gradient* $\partial^2 E(x, \mathbf{p}) / \partial x \partial p_i |_{\mathbf{p}=\mathbf{p}^\circ}$ is not zero. We thus now need the wave-function linear-response vector.

Note that we need only the first-order derivative of the wave function to calculate the second-order derivative of the energy. More generally, we have the so-called *2n + 1 rule*: For variational parameters, the derivatives of the wave function to order n determine the energy derivatives to order $2n + 1$.

Linear response equations

In order to obtain the wave-function linear-response vector $\partial p_i^\circ / \partial x$ in the case where all the parameters are variational, we start by noting that the stationary condition is true *for all x*

$$\forall x, \left. \frac{\partial E(x, \mathbf{p})}{\partial p_i} \right|_{\mathbf{p}=\mathbf{p}^\circ} = 0, \quad (25)$$

which means that we can take the first-order derivative of Eq. (25) with respect to x , giving

$$\left. \frac{\partial^2 E(x, \mathbf{p})}{\partial x \partial p_i} \right|_{\mathbf{p}=\mathbf{p}^\circ} + \sum_j \left. \frac{\partial^2 E(x, \mathbf{p})}{\partial p_i \partial p_j} \right|_{\mathbf{p}=\mathbf{p}^\circ} \frac{\partial p_j^\circ}{\partial x} = 0. \quad (26)$$

We thus arrive at the *linear response equations*

$$\sum_j \frac{\partial^2 E(x, \mathbf{p})}{\partial p_i \partial p_j} \Big|_{\mathbf{p}=\mathbf{p}^0} \frac{\partial p_j^0}{\partial x} = - \frac{\partial^2 E(x, \mathbf{p})}{\partial x \partial p_i} \Big|_{\mathbf{p}=\mathbf{p}^0}, \quad (27)$$

which is a linear system of equations whose solution gives the wave-function linear-response vector $\partial p_i^0 / \partial x$. Remember that, in practice, we are interested in energy derivatives evaluated at $x = 0$. Therefore, these equations must in fact be solved using the unperturbed *electronic Hessian* $\partial^2 E(x = 0, \mathbf{p}) / \partial p_i \partial p_j$ (independent of the perturbation). Since its dimensions are usually large, the response equations are usually solved iteratively without explicitly constructing and storing the Hessian matrix.

Remark: Lagrangian formalism for non-variational parameters

For methods with non-variational parameters (CI, CC, MP2, ...), we can simplify the calculation by using the technique of Lagrange’s multipliers. Let us consider the case of CI with parameters $\mathbf{p} = (\mathbf{c}, \boldsymbol{\kappa})$ where \mathbf{c} are the coefficients of the configurations which are variational, and $\boldsymbol{\kappa}$ are the orbital rotation parameters which are non variational. Indeed, the orbital rotation parameters makes the HF energy stationary, $\partial E_{\text{HF}}(x, \boldsymbol{\kappa}) / \partial \kappa_i = 0$, but not the CI energy, $\partial E_{\text{CI}}(x, \mathbf{c}, \boldsymbol{\kappa}) / \partial \kappa_i \neq 0$. In this case, we define the Lagrange function $L_{\text{CI}}(x, \mathbf{c}, \boldsymbol{\kappa}, \bar{\boldsymbol{\kappa}})$ depending on Lagrange’s multipliers $\bar{\boldsymbol{\kappa}}$

$$L_{\text{CI}}(x, \mathbf{c}, \boldsymbol{\kappa}, \bar{\boldsymbol{\kappa}}) = E_{\text{CI}}(x, \mathbf{c}, \boldsymbol{\kappa}) + \sum_i \bar{\kappa}_i \frac{\partial E_{\text{HF}}(x, \boldsymbol{\kappa})}{\partial \kappa_i}. \quad (28)$$

For all values of x , $L_{\text{CI}}(x, \mathbf{c}, \boldsymbol{\kappa}, \bar{\boldsymbol{\kappa}})$ takes the same value than $E_{\text{CI}}(x, \mathbf{c}, \boldsymbol{\kappa})$, but $L_{\text{CI}}(x, \mathbf{c}, \boldsymbol{\kappa}, \bar{\boldsymbol{\kappa}})$ has the advantage of being stationary with respect to all parameters \mathbf{c} , $\boldsymbol{\kappa}$ and $\bar{\boldsymbol{\kappa}}$. This simplifies the calculation of the derivatives with respect to x , at the price of determining the Lagrange’s multipliers $\bar{\boldsymbol{\kappa}}$.

1.4 Example of linear-response equations for Hartree-Fock: Coupled-perturbed Hartree-Fock

1.4.1 Exponential parametrization

For optimizing the orbitals in the HF determinant wave function, it is convenient to use an exponential parametrization

$$|\Phi(\boldsymbol{\kappa})\rangle = e^{\hat{\kappa}} |\Phi_0\rangle, \quad (29)$$

where $e^{\hat{\kappa}}$ is an unitary operator performing rotations between occupied and virtual spin orbitals in a reference determinant wave function Φ_0 . This rotation operator is constructed from an anti-Hermitian single-excitation operator, $\hat{\kappa} = -\hat{\kappa}^\dagger$, which can be written in the second-quantization formalism as

$$\hat{\kappa} = \sum_a^{\text{occ}} \sum_r^{\text{vir}} \left(\kappa_{ar} \hat{a}_r^\dagger \hat{a}_a - \kappa_{ar}^* \hat{a}_a^\dagger \hat{a}_r \right), \quad (30)$$

where \hat{a}_k^\dagger and \hat{a}_k are the creation and annihilation operators of the spin orbital k , respectively, and the indices a and r refer to occupied and virtual spin orbitals in the reference determinant, respectively. The parameters $\boldsymbol{\kappa} = \{\kappa_{ar}\}$ are called the *orbital rotation parameters*. In comparison to the orbital coefficients on the atomic basis functions, the orbital rotation parameters have the advantage of providing a non-redundant parametrization of the wave function, so that one can vary them independently without having to impose any constraints.

At each step of the optimization, the orbitals in the reference determinant Φ_0 are updated so that one always considers variations of the orbital rotation parameters around $\boldsymbol{\kappa} = \mathbf{0}$. The expansion of the HF wave function with respect to $\boldsymbol{\kappa}$ thus writes

$$\begin{aligned} |\Phi(\boldsymbol{\kappa})\rangle &= \left(\hat{1} + \hat{\kappa} + \frac{1}{2}\hat{\kappa}^2 + \dots \right) |\Phi_0\rangle \\ &= |\Phi_0\rangle + \sum_a^{\text{occ}} \sum_r^{\text{vir}} \kappa_{ar} |\Phi_a^r\rangle \\ &\quad + \left[\frac{1}{2} \sum_a^{\text{occ}} \sum_b^{\text{occ}} \sum_r^{\text{vir}} \sum_s^{\text{vir}} \kappa_{ar} \kappa_{bs} |\Phi_{ab}^{rs}\rangle - \frac{1}{2} \sum_a^{\text{occ}} \sum_r^{\text{vir}} \kappa_{ar} \kappa_{ar}^* |\Phi_0\rangle \right] + \dots, \end{aligned} \quad (31)$$

where $|\Phi_a^r\rangle = \hat{a}_r^\dagger \hat{a}_a |\Phi_0\rangle$ is a singly excited determinant and $|\Phi_{ab}^{rs}\rangle = \hat{a}_r^\dagger \hat{a}_a \hat{a}_s^\dagger \hat{a}_b |\Phi_0\rangle$ is a doubly excited determinant. Note that $|\Phi_{ab}^{rs}\rangle = 0$ if $a = b$ or $r = s$, since a given spin orbital cannot be annihilated or created more than once.

1.4.2 Electronic gradient and Hessian

We now want to calculate the HF electronic gradient and Hessian, i.e. the first- and second-order derivatives of the HF total energy

$$E_{\text{HF}}(\boldsymbol{\kappa}) = \frac{\langle \Phi(\boldsymbol{\kappa}) | \hat{H}_0 | \Phi(\boldsymbol{\kappa}) \rangle}{\langle \Phi(\boldsymbol{\kappa}) | \Phi(\boldsymbol{\kappa}) \rangle} \quad (32)$$

with respect to the parameters $\boldsymbol{\kappa}$. Here, we will only consider the case of real-valued orbitals and real-valued orbital parameters $\kappa_{ar}^* = \kappa_{ar}$. In this case, from Eq. (31), the first- and second-order derivatives of the HF wave function $|\Phi(\boldsymbol{\kappa})\rangle$ are

$$\left. \frac{\partial |\Phi(\boldsymbol{\kappa})\rangle}{\partial \kappa_{ar}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = |\Phi_a^r\rangle, \quad (33)$$

and

$$\left. \frac{\partial^2 |\Phi(\boldsymbol{\kappa})\rangle}{\partial \kappa_{ar} \partial \kappa_{bs}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = |\tilde{\Phi}_{ab}^{rs}\rangle = \begin{cases} |\Phi_{ab}^{rs}\rangle & \text{if } a \neq b \text{ or } r \neq s \\ -|\Phi_0\rangle & \text{if } a = b \text{ and } r = s. \end{cases} \quad (34)$$

Exercise: Assuming the reference wave function Φ_0 is normalized, $\langle \Phi_0 | \Phi_0 \rangle = 1$, show that the HF electronic gradient writes

$$\left. \frac{\partial E_{\text{HF}}}{\partial \kappa_{ar}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = 2 \langle \Phi_a^r | \hat{H}_0 | \Phi_0 \rangle, \quad (35)$$

and is thus zero for converged HF spin orbitals (Brillouin's theorem). Also show that the HF electronic Hessian writes

$$\left. \frac{\partial^2 E_{\text{HF}}}{\partial \kappa_{ar} \partial \kappa_{bs}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = 2 (A_{ar,bs} + B_{ar,bs}), \quad (36)$$

with $A_{ar,bs} = \langle \Phi_a^r | \hat{H}_0 - E_{\text{HF}} | \Phi_b^s \rangle$ and $B_{ar,bs} = \langle \tilde{\Phi}_{ab}^{rs} | \hat{H}_0 - E_{\text{HF}} | \Phi_0 \rangle = \langle \Phi_{ab}^{rs} | \hat{H}_0 | \Phi_0 \rangle$.

Exercise: Using the Slater-Condon rules for calculating expectation values of operators over Slater determinants, show that

$$A_{ar,bs} = (\varepsilon_r - \varepsilon_a) \delta_{ab} \delta_{rs} + \langle rb || as \rangle, \quad (37)$$

and

$$B_{ar,bs} = \langle rs||ab \rangle, \quad (38)$$

where ε_k is the energy of the HF spin orbital k , and $\langle rb||as \rangle = \langle rb|as \rangle - \langle rb|sa \rangle$ are the anti-symmetrized two-electron integrals over the HF spin orbitals.

1.4.3 Example: Calculation of the electric dipole polarizability

The so-called *coupled-perturbed Hartree-Fock (CPHF)* electric dipole polarizability is, according to Eq. (24),

$$\alpha_{i,j}^{\text{CPHF}} = - \left. \frac{\partial^2 \mathcal{E}_{\text{HF}}}{\partial E_i \partial E_j} \right|_{\mathbf{E}=\mathbf{0}} = - \left[\frac{\partial^2 E_{\text{HF}}}{\partial E_i \partial E_j} + \sum_a^{\text{occ}} \sum_r^{\text{vir}} \frac{\partial^2 E_{\text{HF}}}{\partial E_i \partial \kappa_{ar}} \bigg|_{\kappa=\mathbf{0}} \frac{\partial \kappa_{ar}}{\partial E_j} \right], \quad (39)$$

where in this expression E_{HF} is the HF energy in the presence of a perturbing uniform electric field \mathbf{E}

$$E_{\text{HF}}(\mathbf{E}, \kappa) = \frac{\langle \Phi(\kappa) | \hat{H}_0 - \hat{\boldsymbol{\mu}} \cdot \mathbf{E} | \Phi(\kappa) \rangle}{\langle \Phi(\kappa) | \Phi(\kappa) \rangle}, \quad (40)$$

where $\hat{\boldsymbol{\mu}}$ is the dipole moment operator.

Clearly, since the explicit dependence of HF energy on the electric field is linear, we have $\partial^2 E_{\text{HF}} / \partial E_i \partial E_j = 0$. Similarly to the calculation leading to Eq. (35), the HF perturbed electronic gradient is found to be

$$\left. \frac{\partial^2 E_{\text{HF}}}{\partial E_i \partial \kappa_{ar}} \right|_{\kappa=\mathbf{0}} = -2 \langle \Phi_a^r | \hat{\mu}_i | \Phi_0 \rangle = -2 \langle r | \hat{\mu}_i | a \rangle, \quad (41)$$

where $\langle r | \hat{\mu}_i | a \rangle$ are the transition dipole moment one-electron integrals. Therefore, Eq. (39) gives

$$\alpha_{i,j}^{\text{CPHF}} = \sum_a^{\text{occ}} \sum_r^{\text{vir}} 2 \langle r | \hat{\mu}_i | a \rangle \frac{\partial \kappa_{ar}}{\partial E_j}, \quad (42)$$

and it only remains to calculate the wave-function linear-response vector $\partial \kappa_{ar} / \partial E_j$. This requires the resolution of the *HF linear-response equations*, also known as the CPHF equations, which write, using Eqs. (27), (36) and (41),

$$\sum_b^{\text{occ}} \sum_s^{\text{vir}} (A_{ar,bs} + B_{ar,bs}) \frac{\partial \kappa_{bs}}{\partial E_j} = \langle r | \hat{\mu}_j | a \rangle. \quad (43)$$

Using vector/matrix notations, the CPHF electric dipole polarizability finally writes

$$\alpha_{i,j}^{\text{CPHF}} = 2 \boldsymbol{\mu}_i^{\text{T}} (\mathbf{A} + \mathbf{B})^{-1} \boldsymbol{\mu}_j, \quad (44)$$

where $\boldsymbol{\mu}_i$ is the vector of components $\mu_{i,ar} = \langle r | \hat{\mu}_i | a \rangle$ and $\mathbf{A} + \mathbf{B}$ is the matrix of elements $A_{ar,bs} + B_{ar,bs}$.

Remark: The non-interacting case: Uncoupled Hartree-Fock

In the simplified case of no electron-electron interaction, also called *uncoupled Hartree-Fock (UCHF)* in this context, we have $A_{ar,bs} = (\varepsilon_r - \varepsilon_a) \delta_{ab} \delta_{rs}$ and $B_{ar,bs} = 0$. Therefore, Eq. (44) becomes

$$\alpha_{i,j}^{\text{UCHF}} = 2 \sum_a^{\text{occ}} \sum_r^{\text{vir}} \frac{\langle r | \hat{\mu}_i | a \rangle \langle a | \hat{\mu}_j | r \rangle}{\varepsilon_r - \varepsilon_a}. \quad (45)$$

This simple expression is convenient for discussing the physical contents of the polarizability. Indeed, it is clearly seen that the UCHF static dipole polarizability is proportional to the transition dipole-moment integrals $\langle r | \hat{\mu}_i | a \rangle$ and inversely proportional to the (non-interacting) excitation energies $\varepsilon_r - \varepsilon_a$. Therefore, we expect the polarizability to be large for systems with low-lying excited states that can be reached from the ground-state by dipole-allowed transitions. For example, alkaline-earth atoms (Be, Mg, Ca, ...) with their low-lying 2p orbitals have much larger polarizabilities than the rare-gas atoms (He, Ne, Ar, Kr, ...) which have large gaps.

Examples of spherically averaged static dipole polarizabilities $\bar{\alpha} = (\alpha_{x,x} + \alpha_{y,y} + \alpha_{z,z})/3$ for rare-gas and alkaline-earth-metal atoms calculated at the UCHF and CPHF levels are given in Table 1. The polarizabilities are indeed one order of magnitude larger for alkaline-earth-metal atoms than for rare-gas atoms. The CPHF polarizabilities are in relatively good agreement with the estimated exact values for the rare-gas atoms. The UCHF or CPHF polarizabilities are less accurate for alkaline-earth-metal atoms. This is due to the neglect of electron correlation effects, which are particularly large in these systems because of their small HF-orbital gaps.

| | UCHF | CPHF | Estimated exact |
|----|------|------|-----------------|
| He | 1.00 | 1.32 | 1.383 |
| Ne | 1.98 | 2.38 | 2.669 |
| Ar | 10.1 | 10.8 | 11.08 |
| Kr | 15.9 | 16.5 | 16.79 |
| Be | 30.6 | 45.6 | 37.76 |
| Mg | 55.2 | 81.6 | 71.26 |
| Ca | 125 | 185 | 157.1 |

Table 1: Spherically averaged static dipole polarizability $\bar{\alpha} = (\alpha_{x,x} + \alpha_{y,y} + \alpha_{z,z})/3$ (in bohr³) for rare-gas and alkaline-earth-metal atoms calculated at the UCHF and CPHF levels with uncontracted d-aug-cc-pCV5Z basis sets. Table extracted from Ref. [5].

2 Time-dependent molecular properties

2.1 Time-dependent Schrödinger equation and quasi-energy

We now consider a time-dependent Hamiltonian with a periodic time-dependent perturbation operator of the form

$$\hat{H}(t) = \hat{H}_0 + x_1 \hat{V}_1 e^{-i\omega t} + x_2 \hat{V}_2 e^{+i\omega t}, \quad (46)$$

where \hat{H}_0 is still the time-independent unperturbed Hamiltonian, x_1 and x_2 are (real-valued) variables representing the strengths of each perturbation term, and ω is the pulsation (or frequency). For the perturbation operator to be Hermitian, we must impose the condition $\hat{V}_1 = \hat{V}_2^\dagger$ and note that we will ultimately be interested in the case $x_1 = x_2$. Think of this perturbation as representing the interaction of a molecule with a monochromatic electromagnetic field. The time-dependent wave function $\bar{\Psi}(t)$ of this system satisfies the time-dependent Schrödinger equation

$$\left[\hat{H}(t) - i \frac{\partial}{\partial t} \right] |\bar{\Psi}(t)\rangle = 0. \quad (47)$$

This equation can be reformulated in a more convenient form. We first extract a phase factor $\mathcal{F}(t)$ out of the wave function

$$|\bar{\Psi}(t)\rangle = e^{-i\mathcal{F}(t)} |\Psi(t)\rangle, \quad (48)$$

where $\Psi(t)$ is a new time-dependent wave function which satisfies the equation

$$\left[\hat{H}(t) - i \frac{\partial}{\partial t} \right] |\Psi(t)\rangle = \dot{\mathcal{F}}(t) |\Psi(t)\rangle, \quad (49)$$

where $\dot{\mathcal{F}}(t) = d\mathcal{F}/dt$. Equation (49) is in the form of an eigenvalue equation, similar to the time-independent Schrödinger equation, and $\dot{\mathcal{F}}(t)$ plays a role similar to the energy. As the Hamiltonian is time periodic, $\hat{H}(t+T) = \hat{H}(t)$ where $T = 2\pi/\omega$ is the period, we define the *quasi-energy* as the time average of $\dot{\mathcal{F}}(t)$ over a period

$$\mathcal{Q} = \frac{1}{T} \int_0^T dt \dot{\mathcal{F}}(t) = \frac{1}{T} \int_0^T dt \frac{\langle \Psi(t) | \left[\hat{H}(t) - i \frac{\partial}{\partial t} \right] | \Psi(t) \rangle}{\langle \Psi(t) | \Psi(t) \rangle}. \quad (50)$$

The advantage of introducing the quasi-energy is that there is variational principle similar to the time-independent one, namely the exact wave function $\Psi(t)$ solution of Eq. (49) makes \mathcal{Q} stationary with respect to variations in $\Psi(t)$. In the time-independent case, the quasi-energy \mathcal{Q} reduces to the energy \mathcal{E} and the wave function $\Psi(t)$ reduces to the time-independent wave function Ψ .

2.2 Definition of time-dependent molecular properties

The quasi-energy can be expanded with respect to the perturbation parameters x_1 and x_2

$$\mathcal{Q} = \mathcal{Q}^{(0)} + \mathcal{Q}^{(10)} x_1 + \mathcal{Q}^{(01)} x_2 + \frac{1}{2} \mathcal{Q}^{(20)} x_1^2 + \mathcal{Q}^{(11)} x_1 x_2 + \frac{1}{2} \mathcal{Q}^{(02)} x_2^2 + \dots, \quad (51)$$

where $\mathcal{Q}^{(0)} = \langle \Psi_0 | \hat{H}_0 | \Psi_0 \rangle = \mathcal{E}^{(0)} = \mathcal{E}_0$ is the unperturbed energy corresponding to the unperturbed normalized state considered Ψ_0 , and the derivatives

$$\begin{aligned} \mathcal{Q}^{(10)} &= \left. \frac{\partial \mathcal{Q}}{\partial x_1} \right|_{\mathbf{x}=0}; & \mathcal{Q}^{(01)} &= \left. \frac{\partial \mathcal{Q}}{\partial x_2} \right|_{\mathbf{x}=0} \\ \mathcal{Q}^{(20)} &= \left. \frac{\partial^2 \mathcal{Q}}{\partial x_1^2} \right|_{\mathbf{x}=0}; & \mathcal{Q}^{(11)} &= 2 \left. \frac{\partial^2 \mathcal{Q}}{\partial x_1 \partial x_2} \right|_{\mathbf{x}=0}; & \mathcal{Q}^{(02)} &= \left. \frac{\partial^2 \mathcal{Q}}{\partial x_2^2} \right|_{\mathbf{x}=0}; & \text{etc.}, \end{aligned} \quad (52)$$

define *time-dependent molecular properties*. They depend on the frequency ω of the perturbation, and encompass the static molecular properties as a special case for $\omega = 0$.

2.3 Sum-over-state expressions for exact wave functions

Using standard time-dependent perturbation theory on Eq. (49), we obtain the first-order derivative $\mathcal{Q}^{(10)}$

$$\begin{aligned}\mathcal{Q}^{(10)} &= \frac{1}{T} \int_0^T dt \langle \Psi_0 | \hat{V}_1 e^{-i\omega t} | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{V}_1 | \Psi_0 \rangle \delta(\omega),\end{aligned}\quad (53)$$

where we used $(1/T) \int_0^T dt e^{-i\omega t} = \delta(\omega)$. Here, $\delta(\omega)$ must be understood as a Kronecker delta for finite T and as a Dirac delta function for $T \rightarrow \infty$. It is seen that only the static component ($\omega = 0$) is not zero for first-order molecular properties. This can be intuitively understood as follows: We consider molecular properties for a *fixed state* $|\Psi_0\rangle$, and thus ‘‘absorption’’ or ‘‘emission’’ of a photon of frequency $\omega \neq 0$ is not allowed by energy conservation.

Similarly, we find the second-order derivative $\mathcal{Q}^{(20)}$ by perturbation theory on Eq. (49), using intermediate normalization $\langle \Psi_0 | \Psi(t) \rangle = 1$,

$$\mathcal{Q}^{(20)} = \frac{1}{T} \int_0^T dt 2 \langle \Psi_0 | \hat{V}_1 e^{-i\omega t} | \Psi^{(10)}(t) \rangle, \quad (54)$$

where the first-order wave function correction has the form

$$|\Psi^{(10)}(t)\rangle = \sum_{n \neq 0} c_n^{(10)}(t) e^{-i\omega_n t} |\Psi_n\rangle, \quad (55)$$

where $\omega_n = \mathcal{E}_n - \mathcal{E}_0$ are the excitation energies of the unperturbed system, and the first-order coefficients $c_n^{(10)}(t)$ are found using Eq. (49)

$$c_n^{(10)}(t) = -i \int_{-\infty}^t dt' \langle \Psi_n | \hat{V}_1 e^{-i\omega t'} e^{\gamma t'} | \Psi_0 \rangle e^{i\omega_n t'}, \quad (56)$$

where the factor $e^{\gamma t'}$ with $\gamma \rightarrow 0^+$ adiabatically switches on the perturbation from $t' \rightarrow -\infty$, imposing the initial condition $c_n^{(10)}(t \rightarrow -\infty) = 0$. Performing the integration over t' gives

$$c_n^{(10)}(t) = \frac{\langle \Psi_n | \hat{V}_1 e^{-i\omega t} | \Psi_0 \rangle e^{i\omega_n t}}{\omega - \omega_n + i\gamma}, \quad (57)$$

where the factor $e^{\gamma t}$ has been dropped. Combining Eqs. (54), (55) and (57), we find

$$\begin{aligned}\mathcal{Q}^{(20)} &= \frac{1}{T} \int_0^T dt 2 \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{V}_1 e^{-i\omega t} | \Psi_n \rangle \langle \Psi_n | \hat{V}_1 e^{-i\omega t} | \Psi_0 \rangle}{\omega - \omega_n + i\gamma} \\ &= 2 \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{V}_1 | \Psi_n \rangle \langle \Psi_n | \hat{V}_1 | \Psi_0 \rangle}{\omega - \omega_n + i\gamma} \delta(2\omega),\end{aligned}\quad (58)$$

where again only the static component is not zero. The case of the mixed second-order derivative $\mathcal{Q}^{(11)}$ is more interesting. The calculation is similar to the previous one and gives

$$\begin{aligned}\mathcal{Q}^{(11)} &= \frac{1}{T} \int_0^T dt \left[\langle \Psi_0 | \hat{V}_2 e^{+i\omega t} | \Psi^{(10)}(t) \rangle + \langle \Psi_0 | \hat{V}_1 e^{-i\omega t} | \Psi^{(01)}(t) \rangle \right] \\ &= \frac{1}{T} \int_0^T dt \left[\sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{V}_2 e^{+i\omega t} | \Psi_n \rangle \langle \Psi_n | \hat{V}_1 e^{-i\omega t} | \Psi_0 \rangle}{\omega - \omega_n + i\gamma} \right. \\ &\quad \left. + \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{V}_1 e^{-i\omega t} | \Psi_n \rangle \langle \Psi_n | \hat{V}_2 e^{+i\omega t} | \Psi_0 \rangle}{-\omega - \omega_n + i\gamma} \right] \\ &= \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{V}_2 | \Psi_n \rangle \langle \Psi_n | \hat{V}_1 | \Psi_0 \rangle}{\omega - \omega_n + i\gamma} - \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{V}_1 | \Psi_n \rangle \langle \Psi_n | \hat{V}_2 | \Psi_0 \rangle}{\omega + \omega_n - i\gamma},\end{aligned}\quad (59)$$

where we see that $\mathcal{Q}^{(11)}$ does not vanish for $\omega \neq 0$. This is truly a dynamic molecular property. Physically, it corresponds to the following phenomenon: The “absorption” of a (virtual) photon of frequency ω (due to the perturbation $\hat{V}_1 e^{-i\omega t}$) followed by the “emission” of a (virtual) photon of the same frequency (due to the perturbation $\hat{V}_2 e^{+i\omega t}$), which is allowed since there is no net change in energy, probing in the process the excited states of the system. The quantity $\mathcal{Q}^{(11)}$ is called the *linear-response function* of operators \hat{V}_2 and \hat{V}_1 in the spectral representation and it is often denoted as $\mathcal{Q}^{(11)} = \langle\langle \hat{V}_2; \hat{V}_1 \rangle\rangle_\omega$. It can also be seen as giving the change in the expectation value of the operator \hat{V}_2 due to the perturbation $\hat{V}_1 e^{-i\omega t}$. The linear-response function has poles in ω at the excitation energies of the unperturbed system $\omega_n = \mathcal{E}_n - \mathcal{E}_0$ (and at the de-excitation energies $-\omega_n$ for the second term), and hence gives access to all the excitation energies of the system. The infinitesimal imaginary shifts $\pm i\gamma$ are kept because they are important for manipulation of the linear-response function using complex analysis.

Similarly, higher-order derivatives of the quasi-energy \mathcal{Q} leads to quadratic-response functions, cubic-response functions, etc...

Example of the dynamic electric dipole polarizability

The simplest example of a second-order dynamic molecular property is the *dynamic electric dipole polarizability*. We consider the following perturbed Hamiltonian

$$\hat{H}(t) = \hat{H}_0 - \mathbf{E}^+ \cdot \hat{\boldsymbol{\mu}} e^{-i\omega t} - \mathbf{E}^- \cdot \hat{\boldsymbol{\mu}} e^{+i\omega t}, \quad (60)$$

where \mathbf{E}^+ and \mathbf{E}^- are the amplitudes of the oscillating electric field and $\hat{\boldsymbol{\mu}}$ is the dipole-moment operator. The amplitudes \mathbf{E}^+ and \mathbf{E}^- are distinguished for the theoretical derivation but we will eventually be interested in the physical case $\mathbf{E}^+ = \mathbf{E}^- = \mathbf{E}$. The dynamic electric dipole polarizability is then defined as the mixed second-order derivative

$$\alpha_{i,j}(\omega) = - \left. \frac{\partial^2 \mathcal{Q}}{\partial E_i^- \partial E_j^+} \right|_{\mathbf{E}=\mathbf{0}}, \quad (61)$$

where $\mathbf{E} = \mathbf{0}$ refers to $\mathbf{E}^+ = \mathbf{E}^- = \mathbf{0}$. Using Eq. (59) with $\hat{V}_2 = -\hat{\mu}_i$ and $\hat{V}_1 = -\hat{\mu}_j$, we find

$$\alpha_{i,j}(\omega) = - \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{\mu}_i | \Psi_n \rangle \langle \Psi_n | \hat{\mu}_j | \Psi_0 \rangle}{\omega - \omega_n + i\gamma} + \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{\mu}_j | \Psi_n \rangle \langle \Psi_n | \hat{\mu}_i | \Psi_0 \rangle}{\omega + \omega_n - i\gamma}. \quad (62)$$

We are often interested only in the spherical average (or isotropic component) of the polarizability tensor $\bar{\alpha}(\omega) = (1/3) \sum_i \alpha_{i,i}(\omega)$, which can be written as (disregarding the infinitesimal shifts $\pm i\gamma$)

$$\bar{\alpha}(\omega) = \sum_{n \neq 0} \frac{f_n}{\omega_n^2 - \omega^2}, \quad (63)$$

where f_n are the *oscillator strengths*

$$f_n = \frac{2}{3} \omega_n \sum_i |\langle \Psi_0 | \hat{\mu}_i | \Psi_n \rangle|^2. \quad (64)$$

The oscillator strength f_n gives the intensity in the absorption or emission spectrum of the electronic transition from state $|\Psi_0\rangle$ to state $|\Psi_n\rangle$ corresponding to the excitation energy ω_n . The knowledge of the dynamic polarizability $\bar{\alpha}(\omega)$ thus gives access to the full absorption or emission spectrum of the system.

2.4 General expressions for approximate methods

Just like in the static case, the previous expressions of the dynamic molecular properties are not applicable for approximate methods such HF, MCSCF, etc... Due to the analogy between the quasi-energy \mathcal{Q} in the dynamic case and the energy \mathcal{E} in the static case, essentially the same expressions derived in Section 1.3.3 for approximate methods apply here as well.

The quasi-energy \mathcal{Q} is obtained by plugging optimal parameters $\mathbf{p}^\circ(x_1, x_2)$ in a quasi-energy function $Q(x_1, x_2; \mathbf{p})$

$$\mathcal{Q}(x_1, x_2) = Q(x_1, x_2; \mathbf{p}^\circ(x_1, x_2)). \quad (65)$$

In contrast to the static case, the parameters now depend on time and take complex values. They are written as

$$\mathbf{p} = \mathbf{c} e^{-i\omega t} + \mathbf{d}^* e^{+i\omega t}, \quad (66)$$

where \mathbf{c} and \mathbf{d}^* are complex numbers. The complex conjugate \mathbf{d}^* is introduced instead of \mathbf{d} for symmetry reason. We will consider only the case where all the parameters are variational, i.e. fulfilling the stationary conditions

$$\left. \frac{\partial Q}{\partial c_i^*} \right|_{\mathbf{p}=\mathbf{p}^\circ} = 0 \quad \text{and} \quad \left. \frac{\partial Q}{\partial d_i^*} \right|_{\mathbf{p}=\mathbf{p}^\circ} = 0, \quad (67)$$

and similarly for the complex-conjugate equations. Note that the case of non-variational parameters can be treated using the Lagrangian formalism. Thus, only the explicit dependence term contributes to the first-order derivative of the quasi-energy

$$\frac{\partial \mathcal{Q}}{\partial x_1} = \frac{\partial Q}{\partial x_1}, \quad (68)$$

and the second-order derivative of the quasi-energy is

$$\frac{\partial^2 \mathcal{Q}}{\partial x_1 \partial x_2} = \frac{\partial^2 Q}{\partial x_1 \partial x_2} + \sum_i \left(\frac{\partial^2 Q}{\partial x_1 \partial c_i} \frac{\partial c_i}{\partial x_2} + \frac{\partial^2 Q}{\partial x_1 \partial d_i} \frac{\partial d_i}{\partial x_2} + \frac{\partial^2 Q}{\partial x_1 \partial c_i^*} \frac{\partial c_i^*}{\partial x_2} + \frac{\partial^2 Q}{\partial x_1 \partial d_i^*} \frac{\partial d_i^*}{\partial x_2} \right), \quad (69)$$

where it is understood that the parameters are evaluated at their optimal values $\mathbf{p} = \mathbf{p}^\circ$. The *wave-function linear-response vectors* $\partial c_i / \partial x_2$ and $\partial d_i / \partial x_2$ are determined from the *time-dependent linear-response equations*, written in a 2×2 -matrix form,

$$\sum_j \begin{pmatrix} \frac{\partial^2 Q}{\partial c_i^* \partial c_j} & \frac{\partial^2 Q}{\partial c_i^* \partial d_j} \\ \frac{\partial^2 Q}{\partial d_i^* \partial c_j} & \frac{\partial^2 Q}{\partial d_i^* \partial d_j} \end{pmatrix} \begin{pmatrix} \frac{\partial c_j}{\partial x_2} \\ \frac{\partial d_j}{\partial x_2} \end{pmatrix} = - \begin{pmatrix} \frac{\partial^2 Q}{\partial x_2 \partial c_i^*} \\ \frac{\partial^2 Q}{\partial x_2 \partial d_i^*} \end{pmatrix}, \quad (70)$$

where it has been assumed that the terms $\partial^2 Q / \partial c_i^* \partial c_j^*$, $\partial^2 Q / \partial d_i^* \partial d_j^*$, and $\partial^2 Q / \partial c_i^* \partial d_j^*$ vanish. This is indeed normally the case, as it will be illustrated in the next section for time-dependent Hartree-Fock. The linear-response vectors $\partial c_i^* / \partial x_2$ and $\partial d_i^* / \partial x_2$ satisfy a similar equation.

2.5 Example: Time-dependent Hartree-Fock

2.5.1 Time-dependent electronic Hessian

According to Eq. (66), the orbital rotation parameters are written as

$$\boldsymbol{\kappa} = \mathbf{c} e^{-i\omega t} + \mathbf{d}^* e^{+i\omega t}, \quad (71)$$

and we want to calculate the second-order derivatives of the HF quasi-energy

$$Q_{\text{HF}}(\boldsymbol{\kappa}) = \frac{1}{T} \int_0^T dt \frac{\langle \Phi(\boldsymbol{\kappa}) | \hat{H}_0 - i \frac{\partial}{\partial t} | \Phi(\boldsymbol{\kappa}) \rangle}{\langle \Phi(\boldsymbol{\kappa}) | \Phi(\boldsymbol{\kappa}) \rangle}, \quad (72)$$

with respect to the parameters \mathbf{c} , \mathbf{c}^* , \mathbf{d} , and \mathbf{d}^* . We will work out the general case of complex-valued HF orbitals. By plugging the time-dependent parameters of Eq. (71) in the expansion of the HF wave function $|\Phi(\boldsymbol{\kappa})\rangle$ in Eq. (31), we find that the only non-zero first- and second-order derivatives of $|\Phi(\boldsymbol{\kappa})\rangle$ are

$$\left. \frac{\partial |\Phi(\boldsymbol{\kappa})\rangle}{\partial c_{ar}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = e^{-i\omega t} |\Phi_a^r\rangle, \quad (73)$$

$$\left. \frac{\partial |\Phi(\boldsymbol{\kappa})\rangle}{\partial d_{ar}^*} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = e^{+i\omega t} |\Phi_a^r\rangle, \quad (74)$$

and

$$\left. \frac{\partial^2 |\Phi(\boldsymbol{\kappa})\rangle}{\partial c_{ar} \partial c_{bs}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = e^{-2i\omega t} |\Phi_{ab}^{rs}\rangle, \quad (75)$$

$$\left. \frac{\partial^2 |\Phi(\boldsymbol{\kappa})\rangle}{\partial d_{ar}^* \partial d_{bs}^*} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = e^{+2i\omega t} |\Phi_{ab}^{rs}\rangle, \quad (76)$$

$$\left. \frac{\partial^2 |\Phi(\boldsymbol{\kappa})\rangle}{\partial c_{ar} \partial d_{bs}^*} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = \left. \frac{\partial^2 |\Phi(\boldsymbol{\kappa})\rangle}{\partial d_{ar}^* \partial c_{bs}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = |\Phi_{ab}^{rs}\rangle, \quad (77)$$

$$\left. \frac{\partial^2 |\Phi(\boldsymbol{\kappa})\rangle}{\partial c_{ar}^* \partial c_{ar}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = \left. \frac{\partial^2 |\Phi(\boldsymbol{\kappa})\rangle}{\partial d_{ar}^* \partial d_{ar}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = -|\Phi_0\rangle, \quad (78)$$

$$\left. \frac{\partial^2 |\Phi(\boldsymbol{\kappa})\rangle}{\partial c_{ar} \partial d_{ar}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = -e^{-2i\omega t} |\Phi_0\rangle, \quad (79)$$

$$\left. \frac{\partial^2 |\Phi(\boldsymbol{\kappa})\rangle}{\partial c_{ar}^* \partial d_{ar}^*} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = -e^{+2i\omega t} |\Phi_0\rangle. \quad (80)$$

Exercise: By using Eqs. (73)-(80) and performing the time average in Eq. (72), show that the second-order derivatives of the HF quasi-energy are, for $\omega \neq 0$,

$$\left. \frac{\partial^2 Q_{\text{HF}}}{\partial c_{ar}^* \partial c_{bs}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = A_{ar,bs} - \omega S_{ar,bs}, \quad (81)$$

$$\left. \frac{\partial^2 Q_{\text{HF}}}{\partial d_{ar}^* \partial d_{bs}^*} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = A_{ar,bs}^* + \omega S_{ar,bs}^*, \quad (82)$$

$$\left. \frac{\partial^2 Q_{\text{HF}}}{\partial c_{ar}^* \partial d_{bs}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = B_{ar,bs}, \quad (83)$$

$$\left. \frac{\partial^2 Q_{\text{HF}}}{\partial d_{ar}^* \partial c_{bs}} \right|_{\boldsymbol{\kappa}=\mathbf{0}} = B_{ar,bs}^*, \quad (84)$$

where $A_{ar,bs} = \langle \Phi_a^r | \hat{H}_0 - E_{\text{HF}} | \Phi_b^s \rangle = (\varepsilon_r - \varepsilon_a) \delta_{ab} \delta_{rs} + \langle rb || as \rangle$, $B_{ar,bs} = \langle \Phi_{ab}^{rs} | \hat{H}_0 | \Phi_0 \rangle = \langle rs || ab \rangle$ and $S_{ar,bs} = \langle \Phi_a^r | \Phi_b^s \rangle = \delta_{ab} \delta_{rs}$.

2.5.2 Time-dependent linear-response equation

In matrix/vector notations, the time-dependent linear-response equation of Eq. (70) takes the following form in HF

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right] \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = - \begin{pmatrix} \mathbf{V} \\ \mathbf{W} \end{pmatrix}, \quad (85)$$

where \mathbf{A} and \mathbf{B} are the matrices of elements $A_{ar,bs}$ and $B_{ar,bs}$, respectively, $\mathbf{1}$ is the identity matrix, (\mathbf{X}, \mathbf{Y}) is the linear-response vector and (\mathbf{V}, \mathbf{W}) is the perturbed gradient vector. It is interesting to consider the linear-response equation without the right-hand-side perturbation term, which gives the following generalized eigenvalue equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} = \omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}. \quad (86)$$

Note that the matrix \mathbf{A} is Hermitian and the matrix \mathbf{B} is symmetric, and thus the 2×2 -block matrix on the left-hand-side of Eq. (86) is Hermitian. However, the 2×2 -block matrix on the right-hand-side of Eq. (86) is not positive definite. Eq. (86) is not a Hermitian eigenvalue equation but a *pseudo-Hermitian eigenvalue equation*. One can show that if the 2×2 -block matrix on the left-hand-side of Eq. (86) is positive definite then all the eigenvalues ω_n are real numbers. Since this matrix corresponds to the Hessian of the HF energy with respect to the orbital rotation parameters, it is positive definite if the HF solution is a stable minimum with respect to the variation of all orbital parameters. This is known as the *Hartree-Fock stability conditions*.

The solutions of Eq. (86) come in pairs: If $(\mathbf{X}_n, \mathbf{Y}_n)$ is an eigenvector with eigenvalue ω_n , then it is easy to check that $(\mathbf{Y}_n^*, \mathbf{X}_n^*)$ is also an eigenvector with opposite eigenvalue $-\omega_n$. When calculating the dynamic dipole polarizability, we will see that the positive eigenvalues, $\omega_n > 0$, correspond to excitation energies in the time-dependent Hartree-Fock (TDHF) approximation, while the negative eigenvalues, $\omega_n < 0$, correspond to de-excitation energies.

2.5.3 Dynamic dipole polarizability

As a second-order derivative, the TDHF dynamic dipole polarizability is calculated according to Eq. (69)

$$\alpha_{i,j}^{\text{TDHF}}(\omega) = -\frac{\partial^2 Q_{\text{HF}}}{\partial E_i^- \partial E_j^+} = -\left[\frac{\partial^2 Q_{\text{HF}}}{\partial E_i^- \partial E_j^+} + \sum_a^{\text{occ}} \sum_r^{\text{vir}} \frac{\partial^2 Q_{\text{HF}}}{\partial E_i^- \partial c_{ar}} \frac{\partial c_{ar}}{\partial E_j^+} + \frac{\partial^2 Q_{\text{HF}}}{\partial E_i^- \partial d_{ar}} \frac{\partial d_{ar}}{\partial E_j^+} + \sum_a^{\text{occ}} \sum_r^{\text{vir}} \frac{\partial^2 Q_{\text{HF}}}{\partial E_i^- \partial c_{ar}^*} \frac{\partial c_{ar}^*}{\partial E_j^+} + \frac{\partial^2 Q_{\text{HF}}}{\partial E_i^- \partial d_{ar}^*} \frac{\partial d_{ar}^*}{\partial E_j^+} \right], \quad (87)$$

where all the terms are evaluated at $\mathbf{E} = \mathbf{0}$ and $\boldsymbol{\kappa} = \mathbf{0}$. In this expression Q_{HF} is the HF quasi-energy of the perturbed system

$$Q_{\text{HF}}(\mathbf{E}, \boldsymbol{\kappa}) = \frac{1}{T} \int_0^T dt \frac{\langle \Phi(\boldsymbol{\kappa}) | \hat{H}(t) - i \frac{\partial}{\partial t} | \Phi(\boldsymbol{\kappa}) \rangle}{\langle \Phi(\boldsymbol{\kappa}) | \Phi(\boldsymbol{\kappa}) \rangle}, \quad (88)$$

with the Hamiltonian $\hat{H}(t)$ in Eq. (60) which includes the oscillating electric field. As for the static case, the second-order derivative $\partial^2 Q_{\text{HF}} / \partial E_i^- \partial E_j^+$ vanishes, and the first two perturbed gradients in Eq. (87) give the transition dipole-moment integrals

$$\frac{\partial^2 Q_{\text{HF}}}{\partial E_i^- \partial c_{ar}} = -\langle \Phi_0 | \hat{\mu}_i | \Phi_a^r \rangle = -\langle a | \hat{\mu}_i | r \rangle, \quad (89)$$

$$\frac{\partial^2 Q_{\text{HF}}}{\partial E_i^- \partial d_{ar}} = -\langle \Phi_a^r | \hat{\mu}_i | \Phi_0 \rangle = -\langle r | \hat{\mu}_i | a \rangle, \quad (90)$$

the two other terms being zero, $\partial^2 Q_{\text{HF}} / \partial E_i^- \partial c_{ar}^* = \partial^2 Q_{\text{HF}} / \partial E_i^- \partial d_{ar}^* = 0$. This leads to the following expression for the polarizability

$$\alpha_{i,j}^{\text{TDHF}}(\omega) = \begin{pmatrix} \boldsymbol{\mu}_i \\ \boldsymbol{\mu}_i^* \end{pmatrix}^\dagger \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right]^{-1} \begin{pmatrix} \boldsymbol{\mu}_j \\ \boldsymbol{\mu}_j^* \end{pmatrix}, \quad (91)$$

where $\boldsymbol{\mu}_i$ is the vector of elements $\mu_{i,ar} = \langle r | \hat{\mu}_i | a \rangle$.

Exercise: Check that the inverse of the time-dependent Hessian can be written as the following spectral representation:

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right]^{-1} = \sum_n \frac{1}{\omega_n - \omega} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}^\dagger + \frac{1}{\omega_n + \omega} \begin{pmatrix} \mathbf{Y}_n^* \\ \mathbf{X}_n^* \end{pmatrix} \begin{pmatrix} \mathbf{Y}_n^* \\ \mathbf{X}_n^* \end{pmatrix}^\dagger, \quad (92)$$

where the sum is over eigenvectors with positive eigenvalues $\omega_n > 0$ only. The following completeness relation will be assumed:

$$\begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} = \sum_n \begin{pmatrix} \mathbf{X}_n \\ -\mathbf{Y}_n \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}^\dagger - \begin{pmatrix} \mathbf{Y}_n^* \\ -\mathbf{X}_n^* \end{pmatrix} \begin{pmatrix} \mathbf{Y}_n^* \\ \mathbf{X}_n^* \end{pmatrix}^\dagger. \quad (93)$$

Plugging the spectral representation of Eq. (92) into Eq. (91), we finally arrive at, for real-valued HF orbitals,

$$\alpha_{i,j}^{\text{TDHF}}(\omega) = - \sum_n \frac{\boldsymbol{\mu}_i^\text{T} (\mathbf{X}_n + \mathbf{Y}_n) (\mathbf{X}_n + \mathbf{Y}_n)^\text{T} \boldsymbol{\mu}_j}{\omega - \omega_n} + \frac{\boldsymbol{\mu}_i^\text{T} (\mathbf{X}_n + \mathbf{Y}_n) (\mathbf{X}_n + \mathbf{Y}_n)^\text{T} \boldsymbol{\mu}_j}{\omega + \omega_n}. \quad (94)$$

The comparison with the exact expression of the dynamic polarizability in Eq. (62) then confirms that the eigenvalues ω_n in Eq. (86) correspond to excitation energies. The corresponding TDHF oscillator strengths are

$$f_n = \frac{2}{3} \omega_n \sum_i \left[(\mathbf{X}_n + \mathbf{Y}_n)^\text{T} \boldsymbol{\mu}_i \right]^2. \quad (95)$$

2.5.4 Photoabsorption spectrum

TDHF can be used to calculate the discrete part of the photoabsorption spectrum of an electronic system. Indeed, the resolution of the linear-response equation, Eq. (86), directly leads to the excitation energies ω_n from the ground state to state n , and to the associated oscillator strengths f_n (related to the probability of the transitions and therefore to the intensity of the spectrum). Note, however, that linear-response theory does not provide the wave functions of the excited states. This leads to the question of how to assign the calculated excitation energies to a physical state.

It is useful to consider the so-called *Tamm-Dancoff approximation (TDA)* to linear-response theory which corresponds to neglecting the matrix \mathbf{B} in Eq. (86). After setting $\mathbf{B} = \mathbf{0}$, Eq. (86) simplifies to a standard Hermitian eigenvalue equation

$$\mathbf{A} \mathbf{X}_n = \omega_n \mathbf{X}_n, \quad (96)$$

where we recall that \mathbf{A} is the matrix of the Hamiltonian (shifted by the HF energy) in the basis of the single-excited determinants: $A_{ar,bs} = \langle \Phi_a^r | \hat{H}_0 - E_{\text{HF}} | \Phi_b^s \rangle$. Eq. (96) is simply a

configuration-interaction calculation with only single excitations (CIS), whose resolution gives the excited-state wave functions expanded in the basis of single-excited determinants

$$|\Psi_n\rangle = \sum_a^{\text{occ}} \sum_r^{\text{vir}} X_{n,ar} |\Phi_a^r\rangle, \quad (97)$$

and $X_{n,ar}$ is the coefficient for the single orbital excitation $a \rightarrow r$. Thus, in this case, the coefficients \mathbf{X}_n exactly provide the physical contents of the excited state n as contributions of single orbital excitations. Usually, one orbital excitation dominates over all the other orbital excitations, and this is used to assign the state to this orbital excitation. By analogy, in the general linear-response theory case without the TDA, $X_{n,ar} + Y_{n,ar}$ is often taken as an approximation to the coefficient of the wave function of the excited state n on the single-excited determinant Φ_a^r .

Table 2 shows an example of a TDHF calculation of excitation energies and oscillator strengths, without and with the TDA, on the CO molecule. The results are compared with those obtained with time-dependent density-functional theory (TDDFT) with the local-density approximation (LDA), which shares essentially the same formalism, and with a more accurate equation-of-motion coupled-cluster singles doubles (EOM-CCSD) calculation. Experimental values are also given. Due to the difficulty of extracting vertical excitation energies and oscillator strengths from the experimental spectrum, the EOM-CCSD values are taken as reference.

The TDHF excitation energies to the low-lying valence spin-triplet states are very much underestimated, while the TDHF excitation energies to the valence spin-singlet states tend to be more accurate. The TDHF excitation energies to the (diffuse and high-lying) Rydberg states tend to be overestimated. The TDHF underestimation of the excitation energies to the valence spin-triplet states is connected to the so-called *near-triplet Hartree-Fock instability*. This refers to the fact that, for this system, the spin-restricted Hartree-Fock (RHF) ground-state wave function is close to being unstable to spin-triplet variations of the orbitals breaking the spin symmetry. The TDA largely reduces the TDHF underestimation of the excitation energies to the valence spin-triplet states, while not changing much the excitation energies to Rydberg states.

TDLDA does not suffer from near-triplet Hartree-Fock instability and overall gives more accurate valence excitation energies than TDHF. However, the TDLDA Rydberg excitation energies are much too low and pollute the valence spectrum. This is related to the fact that the LDA ionization energy, given by the opposite of the HOMO orbital ($I = -\epsilon_{\text{HOMO}}$), is much too low. The somewhat opposite behaviors of TDHF and TDLDA suggest that more accurate valence and Rydberg excitation energies can be obtained with a proper combination of these two approaches. This is what is effectively done in TDDFT using (range-separated) hybrid functionals.

| State | Transition | TDHF | TDHF-TDA | TDLDA | TDLDA-TDA | EOM-CCSD | Expt |
|--|-------------------------------|-------|----------|--------------|--------------|----------|-------|
| Valence excitation energies (eV) | | | | | | | |
| $^3\Pi$ | $5\sigma \rightarrow 2\pi^*$ | 5.28 | 5.85 | 5.95 | 6.04 | 6.45 | 6.32 |
| $^3\Sigma^+$ | $1\pi \rightarrow 2\pi^*$ | 6.33 | 7.79 | 8.38 | 8.54 | 8.42 | 8.51 |
| $^1\Pi$ | $5\sigma \rightarrow 2\pi^*$ | 8.80 | 9.08 | 8.18 | 8.42 | 8.76 | 8.51 |
| $^3\Delta$ | $1\pi \rightarrow 2\pi^*$ | 7.87 | 8.74 | <i>9.16</i> | <i>9.20</i> | 9.39 | 9.36 |
| $^3\Sigma^-$ | $1\pi \rightarrow 2\pi^*$ | 9.37 | 9.73 | <i>9.84</i> | <i>9.84</i> | 9.97 | 9.88 |
| $^1\Sigma^-$ | $1\pi \rightarrow 2\pi^*$ | 9.37 | 9.73 | <i>9.84</i> | <i>9.84</i> | 10.19 | 9.88 |
| $^1\Delta$ | $1\pi \rightarrow 2\pi^*$ | 9.96 | 10.15 | <i>10.31</i> | <i>10.33</i> | 10.31 | 10.23 |
| $^3\Pi$ | $4\sigma \rightarrow 2\pi^*$ | 13.05 | 13.31 | <i>11.40</i> | <i>11.43</i> | 12.49 | |
| Rydberg excitation energies (eV) | | | | | | | |
| $^3\Sigma^+$ | $5\sigma \rightarrow 6\sigma$ | 11.07 | 11.18 | <i>9.55</i> | <i>9.56</i> | 10.60 | 10.40 |
| $^1\Sigma^+$ | $5\sigma \rightarrow 6\sigma$ | 12.23 | 12.27 | <i>9.93</i> | <i>9.95</i> | 11.15 | 10.78 |
| $^3\Sigma^+$ | $5\sigma \rightarrow 7\sigma$ | 12.40 | 12.42 | <i>10.26</i> | <i>10.26</i> | 11.42 | 11.30 |
| $^1\Sigma^+$ | $5\sigma \rightarrow 7\sigma$ | 12.78 | 12.79 | <i>10.47</i> | <i>10.50</i> | 11.64 | 11.40 |
| $^3\Pi$ | $5\sigma \rightarrow 3\pi$ | 12.52 | 12.60 | <i>10.39</i> | <i>10.39</i> | 11.66 | 11.55 |
| $^1\Pi$ | $5\sigma \rightarrow 3\pi$ | 12.87 | 12.88 | <i>10.48</i> | <i>10.50</i> | 11.84 | 11.53 |
| Ionization threshold: $-\epsilon_{\text{HOMO}}$ (eV) | | | | | | | |
| | | 15.11 | 15.11 | 9.12 | 9.12 | | 15.58 |
| MAD of excitation energies with respect to EOM-CCSD (eV) | | | | | | | |
| Valence | | 0.89 | 0.49 | 0.37 | 0.33 | | |
| Rydberg | | 0.93 | 0.97 | 1.21 | 1.19 | | |
| Total | | 0.91 | 0.69 | 0.73 | 0.70 | | |
| Oscillator strengths ($\times 10^{-2}$) | | | | | | | |
| $^1\Pi$ | $5\sigma \rightarrow 2\pi^*$ | 8.55 | 11.48 | 8.69 | 11.41 | 8.66 | |
| $^1\Sigma^+$ | $5\sigma \rightarrow 6\sigma$ | 10.58 | 10.49 | 1.84 | 2.36 | 0.58 | |
| $^1\Sigma^+$ | $5\sigma \rightarrow 7\sigma$ | 9.39 | 10.22 | 12.53 | 12.25 | 20.71 | |
| $^1\Pi$ | $5\sigma \rightarrow 3\pi$ | 5.13 | 4.94 | 2.71 | 2.16 | 4.94 | |

Table 2: Excitation energies and oscillator strengths of the CO molecule calculated by TDHF and TDLDA, without and with the Tamm-Dancoff approximation (TDA), and by EOM-CCSD, using the Sadlej+ basis set. Excitation energies above the ionization threshold are indicated in italics. Mean absolute deviations (MADs) are calculated with respect to the EOM-CCSD values. Experimental values are also given for comparison. Adapted from Ref. [6].

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