Coupled-perturbed SCF

1 Standard HF SFC

We consider standard closed-shell Hartree-Fock Self-Consistent-Field (HF-SCF) calculations.

MO LCAO orbitals [1]

$$\phi_i = \sum_\nu c_{\nu i}\chi_\nu. \tag{1}$$

Standard HF equations:

$$\sum_\nu c_{\nu i}(f_{\mu\nu} - S_{\mu\nu}\varepsilon_i) = 0, \tag{2}$$

where

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} D_{\rho\sigma}\left(\langle\mu\sigma|\nu\rho\rangle - \frac{1}{2}\langle\mu\sigma|\rho\nu\rangle\right), \tag{3}$$

as the closed-shell AO density matrix, $h_{\mu\nu}$ as the one-electron integrals, and $\langle\mu\sigma|\nu\rho\rangle$ as the two-electron integrals in Dirac notation.

The following energy expression is obtained for this case:

$$E_{HF} = \sum_{\mu\nu} D_{\mu\nu}h_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\,\rho\sigma} D_{\mu\nu}D_{\rho\sigma}\left(\langle\mu\sigma|\nu\rho\rangle - \langle\mu\sigma|\rho\nu\rangle\right), \tag{4}$$

where $D_{\mu\nu}$ is the the density matrix

$$D_{\mu\nu} = 2\sum_i c_{\mu i}^* c_{\nu i}, \tag{5}$$

2 Properties as a response

Properties can be described as a *response of the molecular system to an external perturbation* $\vec{P}$.

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[1] Greek indices are used here and in the following to denote AOs.

A Taylor expansion of system energy around the the «perturbation-free» ($\vec{P} = 0$) yields:

$$E = E_0 + \left.\frac{dE}{d\vec{P}}\right|_{\vec{P}=0} \vec{P} + \frac{1}{2}\left.\frac{d^2E}{d\vec{P}^2}\right|_{\vec{P}=0} \vec{P}^2 + ...$$

Let us consider as an example a molecule in an external electrical field $\vec{\mathcal{E}}$. If we treat the field as a weak perturbation, a Taylor expansion around the the «field-free» ($\vec{\mathcal{E}} = 0$) case is a good description and yields for the energy:

$$E = E_0 + \sum_i^3 \left.\frac{dE}{d\mathcal{E}_i}\right|_{\vec{\mathcal{E}}=0} \mathcal{E}_i + \frac{1}{2}\sum_i^3\sum_j^3 \left.\frac{d^2E}{d\mathcal{E}_i d\mathcal{E}_j}\right|_{\vec{\mathcal{E}}=0} \mathcal{E}_i\mathcal{E}_j + ...,$$

where dipole moment

$$\mu_i = -\left(\frac{\partial E}{\partial \mathcal{E}_i}\right)_{\vec{\mathcal{E}}=0},$$

and polarizability tensor

$$\alpha_{ij} = -\left(\frac{\partial^2 E}{\partial \mathcal{E}_i \mathcal{E}_j}\right)_{\vec{\mathcal{E}}=0}.$$

So, to determine the properties of a molecule in the ground state, we need to somehow find the energy derivatives with respect to the corresponding fields. Common examples include derivatives of the energy with respect to the nuclear displacement or charge displacement, an external electric field, an external magnetic field, or nuclear magnetic moments.

To find the properties of the system, we need to know the dependence of energy on external conditions:

$$E(\vec{P}) = \frac{\left\langle \Phi(\vec{P})\right| \hat{H}(\vec{P}) \left|\Phi(\vec{P})\right\rangle}{\left\langle \Phi(\vec{P})|\Phi(\vec{P})\right\rangle}, \tag{6}$$

where $\hat{H} = \hat{H}_0 + \hat{H}^{(1)}(\vec{P}) + ...$. $\hat{H}_0$ is unperturbed Hamiltonian.

Routine and efficient computation of the various atomic and molecular properties *requires techniques which go beyond* the solution of the HF SFC equation.

> *Clearly, energy and wavefunctions obtained from the solution of the (electronic) HF SFC equation are not sufficient for this purpose, and it is necessary to compute further quantities which characterize the atomic or molecular system of interest.*

To calculate analytical derivatives of the energy $E(\vec{P})$, it is necessary to evaluate the derivatives of the one- and two-electron integrals; this in turn requires evaluation of derivatives of the basis set functions with respect to $\vec{P}$:

$$\frac{d\phi_i(\vec{P})}{d\vec{P}} = \sum_\nu \left(\frac{dc_{\nu i}}{d\vec{P}} \chi_\nu + c_{\nu i} \frac{d\chi_\nu}{d\vec{P}} \right) \tag{7}$$

Thus in order to calculate the energy derivatives, it is necessary to know the quantities $\dfrac{dc_{\nu i}}{d\vec{P}}$ and $\dfrac{d\chi_\nu}{d\vec{P}}$.

3 Coupled-Perturbed Hartree–Fock

In the coupled-perturbed Hartree–Fock method (CPHF), which was probably derived the first time by Peng (1941) and rederived many times (Stevens et al., 1963; Gerratt and Mills, 1968), second- and higher-order static properties are obtained by solving the Hartree–Fock equations:

$$\hat{f}(\vec{P})\phi_i(\vec{P}) = \varepsilon_i(\vec{P})\phi_i(\vec{P}), \tag{8}$$

self-consistently in the presence of a perturbing field $\vec{P}$ under the condition that the perturbed occupied spin orbitals $\left\langle \phi_i(\vec{P}) | \phi_j(\vec{P}) \right\rangle = \delta_{ij}$ remain orthonormal.

Contrary to the unperturbed Hartree–Fock theory, where the molecular orbitals are expanded in atomic one-electron basis functions (1), one normally expands the perturbed occupied spin orbitals in the set of orthonormalized *unperturbed* molecular spin orbitals $\{\phi_p\}$:

$$\phi_i(\vec{P}) = \sum_q^{\text{all}} U_{qi}(\vec{P})\phi_p. \tag{9}$$

Inserting this ansatz in the perturbed Hartree–Fock equations, (9) and (8), multiplying the perturbed Hartree–Fock equations from the left with another basis function, an unperturbed molecular orbital ϕ_r, followed by integration one obtains a matrix form of the perturbed Hartree–Fock equations:

$$\sum_p^{\text{all}} U_{qi}(\vec{P}) \left(F_{rq}(\vec{P}) - \varepsilon_i(\vec{P})\delta_{rq} \right) = 0, \tag{10}$$

where an element of the perturbed Fock matrix $F_{pq}(\vec{P}) = \left\langle \phi_p | \hat{f}(\vec{P}) | \phi_q \right\rangle$:

$$F_{pq}(\vec{P}) = \left\langle \phi_p | \hat{h}(\vec{P}) | \phi_q \right\rangle +$$
$$+ \sum_j^{\text{occ}} \sum_s^{\text{all}} \sum_t^{\text{all}} U_{sj}^*(\vec{P}) \{ \left\langle \phi_p \phi_k | \phi_s \phi_t \right\rangle - \left\langle \phi_p \phi_t | \phi_s \phi_q \right\rangle \} U_{tj}(\vec{P}) \tag{11}$$

4 Derivatives

4.1 First derivative

In the most general approach of quantum chemical methods, the total energy is calculated by optimizing the parameters $c = \{c_1, c_2, ..., c_n\}$ as a function of energy $E = E(\vec{P}, c(\vec{P}))$ for each fixed perturbation value $\vec{P}$. As a result, the total energy for the optimized parameters $c_0(\vec{P})$ is a function of $\vec{P}$:

$$E = E(\vec{P}, c_0(\vec{P})). \tag{12}$$

We now write the first derivative of the energy with respect to the perturbation parameter $\vec{P}$:

$$\frac{dE}{d\vec{P}} = \frac{\partial E(\vec{P}, c_0)}{\partial \vec{P}} + \sum_i \left. \frac{\partial E(\vec{P}, c)}{\partial c_i} \right|_{c=c_0} \frac{\partial c_{0_i}}{\partial \vec{P}} \tag{13}$$

Derivative $\frac{\partial c_{0_i}}{\partial \vec{P}}$ contains information about how the electronic structure changes under perturbation. It is impossible to apply the formula "on the forehead since the explicit dependence $c_{0_i}(\vec{P})$ is unknown. However, when all parameters are variational, then the calculations are significantly simplified since in this case:

$$\left. \frac{\partial E(\vec{P}, c)}{\partial c_i} \right|_{c=c_0} = 0 \tag{14}$$

due to the fact that the calculations are carried out at a stationary point, then

$$\frac{dE}{d\vec{P}} = \frac{\partial E(\vec{P}, c_0)}{\partial \vec{P}}, \tag{15}$$

therefore, it is not necessary to know the $\frac{\partial c_{0_i}}{\partial \vec{P}}$.

> *A good example is the calculation of the molecular gradient at the level of HF theory, where we only need to know the explicit dependence of the Hamiltonian and the wave functions of nuclear coordinates, but not in the knowledge of the implicit dependence of the orbital coefficients on nuclear coordinates, since all these parameters are variable.*

4.2 Second derivative

$$\frac{d^2 E}{d\vec{P}^2} = \frac{\partial^2 E(\vec{P}, c_0)}{\partial \vec{P}^2} + \sum_i \left. \frac{\partial^2 E(\vec{P}, c)}{\partial \vec{P} \partial c_i} \right|_{c=c_0} \frac{\partial c_{0_i}}{\partial \vec{P}}, \tag{16}$$

where $\left. \dfrac{\partial^2 E(\vec{P}, c)}{\partial \vec{P} \partial c_i} \right|_{c=c_0} \neq 0$, we need to know the $\dfrac{\partial c_{0_i}}{\partial \vec{P}}$.

5   Response equation

Take the derivative from ([14](#)) by $\vec{P}$, we get

$$\sum_j \frac{\partial^2 E(\vec{P}, c)}{\partial c_j \partial c_i}\bigg|_{\substack{\vec{P}=0 \\ c=c_0}} \frac{\partial c_{0_i}}{\partial \vec{P}} = -\frac{\partial^2 E(\vec{P}, c)}{\partial \vec{P} \partial c_i}\bigg|_{c=c_0}. \tag{17}$$

Solution of this system will lead to the calculation $\dfrac{\partial c_{0_i}}{\partial \vec{P}}$.

> *Aber, meine Herren, das ist keine Physik!*