2nd derivatives of the electronic energy in density functional theory

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Abstract

This document details the equations needed to implement the calculation of vibrational frequencies within the density functional formalism of electronic structure theory. This functionality has been incorporated into the CCP1 DFT module and the required changes to the application programmers interface are outlined. Throughout it is assumed that an implementation of Hartree-Fock vibrational frequencies is available that can be modified to incorporate the density functional formalism. Employing GAMESS-UK as an example the required changes to the Hartree-Fock code are outlined.

Contents

Acknowledgements

Conventions

The occupied molecular orbitals are labeled i, j, k, l, and m. The virtual molecular orbitals are labeled a, b, c, d, and e. Arbitrary molecular orbitals are labeled p, q, r, s, and t. Arbitrary atomic orbitals are labeled μ, ν, λ and σ. Molecular orbitals are denoted by ψ, and atomic orbitals are denoted by χ. The superscripts α and β indicate the α-spin and β-spin components of various quantities. The superscripts a and b indicate nuclear coordinates with respect to which derivatives are taken.

Chapter 1

Introduction

The objective of this project is to implement the calculation of vibrational frequencies within the framework of Density Functional Theory (DFT). These properties are essential for classifying stationary points on the potential energy surface as well as determining the vibrational spectrum of a molecule. The implementation of this property is very similar to the implementation of polarisabilities which will be obtained as a side effect at very little cost. In both cases the underlying formalism depends on having the analytic second derivatives of the DFT energy. For the the polarisabilities these derivatives with respect to an external electric field are required. For the vibrational frequencies the more complicated derivatives with respect to the nuclear coordinates are needed. As the latter derivatives are the more general ones we will focus on those in this document. The implementation will take place within the framework of the DFT module developed initially within the Collaborative Computational Project 1 (CCP1) and subsequently extended by the Quantum Chemistry Group at Daresbury.

As far as the implementation is concerned we follow the approach of Handy, Tozer, Laming, Murray, and Amos [4] and Johnson and Fisch [5]. According to Amos it is important that the derivatives of the quadrature are taken into account as well.

In chapter 2 we will first write down the expressions that define the DFT energy. To include the derivatives of the quadrature we will rewrite the appropriate integrals as a quadrature. In chapters 3 and 4 we will take the first and second derivatives of the integral expressions, while the first and second derivatives of the quadrature are considered in chapter 5. Finally, details of the implementation are presented in chapter 6.

Chapter 2

DFT energy

The DFT total energy of a molecular system in the Born-Oppenheimer approximation can be written as a sum of three terms. The first two terms are easily recognised as having a classical origin. They are the kinetic energy and the Coulomb energy of the electrons. The third term stems from the anti-symmetry of the wavefunction and has no classical equivalent. This term is called the exchange-correlation energy. Following Johnson and Fisch [5] we can write the total energy in general as

$$
\begin{aligned}
E &= \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} \\
&+ \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma) \\
&+ E_{xc}(P^{\alpha}, P^{\beta})
\end{aligned}
\tag{2.1}
$$

where

$$
P_{\mu\nu}^{\alpha} = \sum_{i^{\alpha}} C_{\mu i^{\alpha}}^{\alpha} C_{\nu i^{\alpha}}^{\alpha}
\tag{2.2}
$$

$$
P_{\mu\nu}^{\beta} = \sum_{i^{\beta}} C_{\mu i^{\beta}}^{\beta} C_{\nu i^{\beta}}^{\beta}
\tag{2.3}
$$

$$
P = P^{\alpha} + P^{\beta}
\tag{2.4}
$$

are the 1-electron reduced density matrices. The term E_{xc} is the exchange-correlation energy. Within the Hartree-Fock approximation this is

$$
E_{xc}^{HF} = -\frac{1}{2} \sum_{\mu\nu\lambda\sigma} (P_{\mu\nu}^{\alpha} P_{\lambda\sigma}^{\alpha} + P_{\mu\nu}^{\beta} P_{\lambda\sigma}^{\beta})(\mu\lambda|\sigma\nu)
\tag{2.5}
$$

In DFT the exchange-correlation energy is given by a functional of the form

$$
E_{xc}^{KS} = \int f(\rho_{\alpha}, \rho_{\beta}, \gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta}) dr
\tag{2.6}
$$

$$\rho_\alpha \;=\; \sum_{\mu\nu} P^\alpha_{\mu\nu} \chi_\mu \chi_\nu \tag{2.7}$$

$$\rho_\beta \;=\; \sum_{\mu\nu} P^\beta_{\mu\nu} \chi_\mu \chi_\nu \tag{2.8}$$

$$\gamma_{\alpha\alpha} \;=\; \nabla\rho_\alpha \cdot \nabla\rho_\alpha \tag{2.9}$$

$$\gamma_{\alpha\beta} \;=\; \nabla\rho_\alpha \cdot \nabla\rho_\beta \tag{2.10}$$

$$\gamma_{\beta\beta} \;=\; \nabla\rho_\beta \cdot \nabla\rho_\beta \tag{2.11}$$

$$\nabla\rho_\alpha \;=\; \sum_{\mu\nu} P^\alpha_{\mu\nu} \nabla(\chi_\mu \chi_\nu) \tag{2.12}$$

$$\nabla\rho_\beta \;=\; \sum_{\mu\nu} P^\beta_{\mu\nu} \nabla(\chi_\mu \chi_\nu) \tag{2.13}$$

$$\tag{2.14}$$

where we have limited the functional form to the so called Generalised Gradient Approximation (GGA), i.e. the highest order derivative of the density needed to evaluate the functional is the gradient. More advanced schemes are currently being explored but only very few programs can actually use them. How effective these higher order functionals are remains unclear.

Due to the form of the functional f the integration in the above expression cannot be performed analytically, instead a quadrature is introduced. The quadrature we use follows the scheme proposed by Becke [2] where the integrand is partitioned into atomic terms each of which is discretised on an atomic grid in polar coordinates

$$E^{KS}_{xc} \;\approx\; \sum_{Ai} w_{Ai} D_A(r_{Ai})$$
$$\cdot f(\rho_\alpha(r_{Ai}), \rho_\beta(r_{Ai}), \gamma_{\alpha\alpha}(r_{Ai}), \gamma_{\alpha\beta}(r_{Ai}), \gamma_{\beta\beta}(r_{Ai})) \tag{2.15}$$

where D_A is the partition associated with atom A. Note that both r_{Ai} and the partition functions D_A are functions of the molecular geometry. However, because the grid points move along with the atom they are associated with the weights w_{Ai} are independent of the geometry.

Finally the coefficients that appear in the density matrices are essentially the coefficients of the atomic orbitals in the SCF wavefunctions. The SCF wavefunctions satisfy the conditions

$$F^\alpha C^\alpha \;=\; SC^\alpha \epsilon^\alpha \tag{2.16}$$

$$F^\beta C^\beta \;=\; SC^\beta \epsilon^\beta \tag{2.17}$$

$$(C^\alpha)^T SC^\alpha \;=\; 1 \tag{2.18}$$

$$(C^\beta)^T SC^\beta \;=\; 1 \tag{2.19}$$

The Fock-matrices are given by

$$F^\alpha{}_{\mu\nu} \;=\; \frac{\partial E}{\partial P^\alpha_{\mu\nu}} \tag{2.20}$$

$$F^{\beta}{}_{\mu\nu} \quad = \quad \frac{\partial E}{\partial P^{\beta}_{\mu\nu}} \tag{2.21}$$

More explicitly the Fock-matrices are

$$F^{\alpha}{}_{\mu\nu} \quad = \quad H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\nu|\lambda\sigma) + \frac{\partial E_{xc}(P^{\alpha}, P^{\beta})}{\partial P^{\alpha}_{\mu\nu}} \tag{2.22}$$

$$F^{\beta}{}_{\mu\nu} \quad = \quad H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\nu|\lambda\sigma) + \frac{\partial E_{xc}(P^{\alpha}, P^{\beta})}{\partial P^{\beta}_{\mu\nu}} \tag{2.23}$$

Because the Fock-matrices depend on the electron density, while the electron density depends on the orbital coefficients, and the coefficients are solutions of an eigenvalue equation involving the Fock-matrices, it is clear that some iterative solution scheme is required. However, the details of that scheme are not required here. Only the details of the energy expression and the Fock-matrices will feature in our discussion of the Hessians.

Chapter 3

DFT gradient

In the previous section we defined the energy in equation (2.1). Here we will briefly consider the gradient of that energy. Differentiating the energy with respect to a nuclear coordinate R_a we have

$$
\begin{aligned}
\frac{\partial E}{\partial R_a} &= \sum_{\mu\nu} \left(\frac{\partial P_{\mu\nu}}{\partial R_a} H_{\mu\nu} + P_{\mu\nu} \frac{\partial H_{\mu\nu}}{\partial R_a} \right) \\
&+ \sum_{\mu\nu\lambda\sigma} \left(\frac{\partial P_{\mu\nu}}{\partial R_a} P_{\lambda\sigma}(\mu\nu|\lambda\sigma) + \frac{1}{2} P_{\mu\nu} P_{\lambda\sigma} \frac{\partial(\mu\nu|\lambda\sigma)}{\partial R_a} \right) \\
&+ \left. \frac{\partial E_{xc}}{\partial R_a} \right|_{P^\alpha, P^\beta} + \sum_{\mu\nu} \frac{\partial E_{xc}(P^\alpha, P^\beta)}{\partial P^\alpha_{\mu\nu}} \frac{\partial P^\alpha_{\mu\nu}}{\partial R_a} + \sum_{\mu\nu} \frac{\partial E_{xc}(P^\alpha, P^\beta)}{\partial P^\beta_{\mu\nu}} \frac{\partial P^\beta_{\mu\nu}}{\partial R_a} \\
&= \sum_{\mu\nu} P_{\mu\nu} H^a_{\mu\nu} \\
&+ \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma}(\mu\nu|\lambda\sigma)^a \\
&+ E^{(a)}_{xc}(P^\alpha, P^\beta) \\
&+ \sum_{\mu\nu} \left(F^\alpha{}_{\mu\nu} \frac{\partial P^\alpha_{\mu\nu}}{\partial R_a} + F^\beta{}_{\mu\nu} \frac{\partial P^\beta_{\mu\nu}}{\partial R_a} \right)
\end{aligned} \tag{3.1}
$$

where we have introduced a superscript a as a short hand for the differentiation with respect to R_a. The superscript (a) means differentiating all the explicit geometry dependent factors, i.e. leaving out the terms that involve differentiation of the orbital coefficients.

The terms involving the Fock-matrices can be simplified using equations (2.16), (2.17) and the derivative of the orthonormality condition:

$$
0 = \sum_{\mu\nu} \left[\frac{\partial C^\alpha_{\mu i}}{\partial R_a} S_{\mu\nu} C^\alpha_{\nu j} + C^\alpha_{\mu i} \frac{\partial S_{\mu\nu}}{\partial R_a} C^\alpha_{\nu j} + C^\alpha_{\mu i} S_{\mu\nu} \frac{\partial C^\alpha_{\nu j}}{\partial R_a} \right] \tag{3.2}
$$

$$\sum_{\mu\nu} C^{\alpha}_{\mu i} \frac{\partial S_{\mu\nu}}{\partial R_a} C^{\alpha}_{\nu j} = -\sum_{\mu\nu} \left[\frac{\partial C^{\alpha}_{\mu i}}{\partial R_a} S_{\mu\nu} C^{\alpha}_{\nu j} + C^{\alpha}_{\mu i} S_{\mu\nu} \frac{\partial C^{\alpha}_{\nu j}}{\partial R_a} \right] \qquad (3.3)$$

This enables us to write

$$\sum_{\mu\nu} F^{\alpha}{}_{\mu\nu} \frac{\partial P^{\alpha}_{\mu\nu}}{\partial R_a} = \sum_{\mu\nu i} F^{\alpha}{}_{\mu\nu} \frac{\partial C^{\alpha}_{\mu i}}{\partial R_a} C^{\alpha}_{\nu i} + \sum_{\mu\nu i} F^{\alpha}{}_{\mu\nu} C^{\alpha}_{\mu i} \frac{\partial C^{\alpha}_{\nu i}}{\partial R_a} \qquad (3.4)$$

$$= \sum_{\mu\nu i} S_{\mu\nu} \frac{\partial C^{\alpha}_{\mu i}}{\partial R_a} C^{\alpha}_{\nu i} \epsilon^{\alpha}_i + \sum_{\mu\nu i} S_{\mu\nu} C^{\alpha}_{\mu i} \frac{\partial C^{\alpha}_{\nu i}}{\partial R_a} \epsilon^{\alpha}_i \qquad (3.5)$$

$$= -\sum_{\mu\nu i} S^a_{\mu\nu} \epsilon^{\alpha}_i C^{\alpha}_{\mu i} C^{\alpha}_{\nu i} \qquad (3.6)$$

$$= -\sum_{\mu\nu} W^{\alpha}_{\mu\nu} S^a_{\mu\nu} \qquad (3.7)$$

where

$$W^{\alpha}_{\mu\nu} = \sum_i \epsilon^{\alpha}_i C^{\alpha}_{\mu i} C^{\alpha}_{\nu i} \qquad (3.8)$$

$$W_{\mu\nu} = W^{\alpha}_{\mu\nu} + W^{\beta}_{\mu\nu} \qquad (3.9)$$

With this result the gradient of the energy becomes

$$\frac{\partial E}{\partial R_a} = \sum_{\mu\nu} P_{\mu\nu} H^a_{\mu\nu}$$
$$+ \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma)^a$$
$$+ E^{(a)}_{xc}(P^{\alpha}, P^{\beta})$$
$$- \sum_{\mu\nu} W_{\mu\nu} S^a_{\mu\nu} \qquad (3.10)$$

The most notable aspect of this expression is that for the first derivative of the energy no derivatives of the orbital coefficients are required. All quantities needed to evaluate this expression have been coded earlier and thus can be assumed to be available whenever required.

Chapter 4

DFT hessian

The expression for the second derivative of the energy can be obtained from differentiating the gradient expression equation (3.10).

$$
\begin{aligned}
\frac{\partial^2 E}{\partial R_b \partial R_a} &= \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{ab} \\
&+ \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma)^{ab} \\
&+ E^{(a)(b)}(P^\alpha, P^\beta) \\
&- \sum_{\mu\nu} W_{\mu\nu} S_{\mu\nu}^{ab} \\
&+ \sum_{\mu\nu} \left(\frac{\partial P_{\mu\nu}}{\partial R_b} \left[H_{\mu\nu}^a + \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\nu|\lambda\sigma)^a \right] \right) \\
&- \sum_{\mu\nu} \frac{\partial W_{\mu\nu}}{\partial R_b} S_{\mu\nu}^a
\end{aligned}
\tag{4.1}
$$

4.1 The explicit 2nd derivative of the exchange-correlation energy

The first thing we need is an expression for the explicit second derivatives of the exchange-correlation energy. This is

$$
\begin{aligned}
E^{(a)(b)}(P^\alpha, P^\beta) &= \sum_{Ai} w_{Ai} \frac{\partial^2 P_A(r_{Ai})}{\partial R_a \partial R_b} f \\
&+ \sum_{Ai} w_{Ai} \frac{\partial P_A(r_{Ai})}{\partial R_a} f^{(b)} \\
&+ \sum_{Ai} w_{Ai} \frac{\partial P_A(r_{Ai})}{\partial R_b} f^{(a)}
\end{aligned}
$$

$$+ \sum_{Ai} w_{Ai} P_A(r_{Ai}) f^{(a)(b)} \tag{4.2}$$

where

$$f^{(a)} = \sum_{\zeta} \frac{\partial f}{\partial \zeta} \zeta^{(a)} \tag{4.3}$$

$$f^{(a)(b)} = \sum_{\zeta\eta} \frac{\partial^2 f}{\partial \zeta \partial \eta} \zeta^{(a)} \eta^{(b)} + \frac{\partial f}{\partial \zeta} \zeta^{(a)(b)} \tag{4.4}$$

The discussion of the derivatives of the partition function will be postponed until chapter 5 and only the second derivative of the functional will be considered here.

The required gradients of ρ and $\nabla\rho$ have already been coded. The second derivatives of these quantities are still needed.

$$\rho_\alpha^{(a)(b)} = \sum_{\mu\nu} P_{\mu\nu}^\alpha \left(\chi_\mu^{ab} \chi_\nu + \chi_\mu^a \chi_\nu^b + \chi_\mu^b \chi_\nu^a + \chi_\mu \chi_\nu^{ab} \right) \tag{4.5}$$

$$\nabla\rho_\alpha^{(a)(b)} = \sum_{\mu\nu} P_{\mu\nu}^\alpha \left(\nabla\chi_\mu^{ab} \chi_\nu + \nabla\chi_\mu^a \chi_\nu^b + \nabla\chi_\mu^b \chi_\nu^a + \nabla\chi_\mu \chi_\nu^{ab} \right)$$

$$+ \sum_{\mu\nu} P_{\mu\nu}^\alpha \left(\chi_\mu^{ab} \nabla\chi_\nu + \chi_\mu^a \nabla\chi_\nu^b + \chi_\mu^b \nabla\chi_\nu^a + \chi_\mu \nabla\chi_\nu^{ab} \right) \tag{4.6}$$

$$(\nabla\rho_\alpha \cdot \nabla\rho_\alpha)^{(a)(b)} = 2\nabla\rho_\alpha^{(a)(b)} \cdot \nabla\rho_\alpha + 2\nabla\rho_\alpha^{(a)} \cdot \nabla\rho_\alpha^{(b)} \tag{4.7}$$

The various derivatives of the basis functions are given in appendix B.

4.2 Defining the 1st derivative of the orbital co-efficients

Beyond this point we need to find an expression for the derivatives of the orbital coefficients. For this purpose we introduce matrices U that express the gradient of the orbitals as

$$\frac{\partial \psi_p}{\partial R_b} = \sum_q \psi_q U_{qp}^b + \psi_p^{(b)} \tag{4.8}$$

$$\frac{\partial \sum_\mu \chi_\mu C_{\mu p}}{\partial R_b} = \sum_{\mu q} \chi_\mu C_{\mu q} U_{qp}^b + \sum_\mu \chi_\mu^b C_{\mu q} \tag{4.9}$$

$$\frac{\partial C_{\mu p}}{\partial R_b} = \sum_q C_{\mu q} U_{qp}^b \tag{4.10}$$

With this definition we can show by differentiating equation (2.18) that

$$U_{pq}^{\alpha b} + S_{pq}^{(b)} + U_{qp}^{\alpha b} = 0 \tag{4.11}$$

Together with the invariance of the energy for rotations among the occupied orbitals it follows that

$$U_{ij}^{\alpha b} = -\frac{1}{2}S_{ij}^{(b)} \tag{4.12}$$

$$U_{ab}^{\alpha b} = -\frac{1}{2}S_{ab}^{(b)} \tag{4.13}$$

4.3 The 1st derivative of the density matrix and the weighted energy matrix

To evaluate the 2nd derivative expression we still need to know the derivative of $P_{\mu\nu}$ and $W_{\mu\nu}$. These expressions are

$$\frac{\partial P_{\mu\nu}^{\alpha}}{\partial R_b} = -\frac{1}{2}\sum_{ij} S_{ij}^{(b)}\left[C_{\mu j}^{\alpha}C_{\nu i}^{\alpha} + C_{\mu i}^{\alpha}C_{\nu j}^{\alpha}\right]$$

$$+ \sum_{ia} U_{ai}^{\alpha b}\left[C_{\mu a}^{\alpha}C_{\nu i}^{\alpha} + C_{\mu i}^{\alpha}C_{\nu a}^{\alpha}\right] \tag{4.14}$$

$$\frac{\partial W_{\mu\nu}^{\alpha}}{\partial R_b} = \sum_{i}\epsilon_i^{\alpha b}C_{\mu i}^{\alpha}C_{\nu i}^{\alpha} - \sum_{ji}\frac{1}{2}\epsilon_i^{\alpha}S_{ij}^{(b)}\left[C_{\mu j}^{\alpha}C_{\nu i}^{\alpha} + C_{\mu i}^{\alpha}C_{\nu j}^{\alpha}\right]$$

$$+ \sum_{ai}\epsilon_i^{\alpha}U_{ai}^{\alpha b}\left[C_{\mu a}^{\alpha}C_{\nu i}^{\alpha} + C_{\mu i}^{\alpha}C_{\nu a}^{\alpha}\right] \tag{4.15}$$

4.4 The 1st derivative of the orbital energy

First of all the expression for $\epsilon_p^{\alpha b}$ can be obtained by differentiating the stationary condition in the MO-basis:

$$F_{pq}^{\alpha b} = S_{pq}^{\alpha b}\epsilon_q^{\alpha} + S^{\alpha}{}_{pq}\epsilon_q^{\alpha b} \tag{4.16}$$

$$\epsilon_q^{\alpha b} = F_{qq}^{\alpha b} - S_{qq}^{\alpha b}\epsilon_q^{\alpha} \tag{4.17}$$

Given the Fock matrix in the AO-basis in equation (2.22) the Fock matrix in the MO-basis is written as

$$F^{\alpha}{}_{pq} = \sum_{\mu\nu} C_{\mu p}^{\alpha}C_{\nu q}^{\alpha}H_{\mu\nu}$$

$$+ \sum_{\mu\nu\lambda\sigma} C_{\mu p}^{\alpha}C_{\nu q}^{\alpha}P_{\lambda\sigma}(\mu\nu|\lambda\sigma)$$

$$+ \sum_{\mu\nu\lambda\sigma} C_{\mu p}^{\alpha}C_{\nu q}^{\alpha}\frac{\partial E_{xc}(P^{\alpha}, P^{\beta})}{\partial P_{\mu\nu}^{\alpha}} \tag{4.18}$$

Differentiating this with respect to the coordinates of atom B gives:

$$\frac{\partial F^{\alpha}{}_{pq}}{\partial R_b} = \sum_{r} U_{rp}^{\alpha b}H^{\alpha}{}_{rq}$$

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$$+ \quad \sum_r U_{rq}^{\alpha b} H^{\alpha}{}_{pr}$$

$$+ \quad H_{pq}^{\alpha(b)}$$

$$+ \quad \sum_{ri^{\alpha}} U_{rp}^{\alpha b}(rq|i^{\alpha}i^{\alpha})$$

$$+ \quad \sum_{ri^{\alpha}} U_{rq}^{\alpha b}(pr|i^{\alpha}i^{\alpha})$$

$$+ \quad \sum_{r^{\alpha}i^{\alpha}} 2U_{r^{\alpha}i^{\alpha}}^{\alpha b}(pq|r^{\alpha}i^{\alpha})$$

$$+ \quad \sum_{r^{\beta}i^{\beta}} 2U_{r^{\beta}i^{\beta}}^{\beta b}(pq|r^{\beta}i^{\beta})$$

$$+ \quad \sum_{i^{\alpha}} (pq|i^{\alpha}i^{\alpha})^{b}$$

$$+ \quad \sum_r U_{rp}^{\alpha b} Q^{\alpha}{}_{rq}$$

$$+ \quad \sum_r U_{rq}^{\alpha b} Q^{\alpha}{}_{pr}$$

$$+ \quad Q_{pq}^{\alpha(b)}$$

$$+ \quad \sum_{r^{\alpha}} U_{r^{\alpha}i^{\alpha}}^{\alpha b} G_{pqr^{\alpha}i^{\alpha}}^{\alpha\alpha}$$

$$+ \quad \sum_{r^{\beta}} U_{r^{\beta}i^{\beta}}^{\alpha b} G_{pqr^{\beta}i^{\beta}}^{\alpha\beta} \qquad (4.19)$$

where

$$Q^{\alpha}{}_{pq} \;=\; \sum_{\mu\nu} C_{\mu p}^{\alpha} C_{\nu q}^{\alpha} \frac{\partial E_{xc}(P^{\alpha}, P^{\beta})}{\partial P_{\mu\nu}^{\alpha}} \qquad (4.20)$$

$$G_{pqrs}^{\alpha\alpha} \;=\; \sum_{\mu\nu\lambda\sigma} C_{\mu p}^{\alpha} C_{\nu q}^{\alpha}(C_{\lambda r}^{\alpha} C_{\sigma s}^{\alpha} + C_{\lambda s}^{\alpha} C_{\sigma r}^{\alpha}) \frac{\partial^2 E_{xc}(P^{\alpha}, P^{\beta})}{\partial P_{\mu\nu}^{\alpha} \partial P_{\lambda\sigma}^{\alpha}} \qquad (4.21)$$

$$G_{pqrs}^{\alpha\beta} \;=\; \sum_{\mu\nu\lambda\sigma} C_{\mu p}^{\alpha} C_{\nu q}^{\alpha}(C_{\lambda r}^{\beta} C_{\sigma s}^{\beta} + C_{\lambda s}^{\beta} C_{\sigma r}^{\beta}) \frac{\partial^2 E_{xc}(P^{\alpha}, P^{\beta})}{\partial P_{\mu\nu}^{\alpha} \partial P_{\lambda\sigma}^{\beta}} \qquad (4.22)$$

$$\frac{\partial F^{\alpha}{}_{pq}}{\partial R_b} \;=\; \sum_r U_{rp}^{\alpha b}\left(H^{\alpha}{}_{rq} + Q^{\alpha}{}_{rq} + \sum_i^{\alpha}(rq|i^{\alpha}i^{\alpha}) \right)$$

$$+ \quad \sum_r U_{rq}^{\alpha b}\left(H^{\alpha}{}_{pr} + Q^{\alpha}{}_{pr} + \sum_i^{\alpha}(pr|i^{\alpha}i^{\alpha}) \right)$$

$$+ \quad H_{pq}^{\alpha(b)}$$

$$+ \quad \sum_{r^{\alpha}i^{\alpha}} U_{r^{\alpha}i^{\alpha}}^{\alpha b}\left[2(pq|r^{\alpha}i^{\alpha}) + G_{pqr^{\alpha}i^{\alpha}}^{\alpha\alpha} \right]$$

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$$+ \quad \sum_{r^\beta i^\beta} U^{\beta b}_{r^\beta i^\beta} \left[2(pq|r^\beta i^\beta) + G^{\alpha\beta}_{pqr^\beta i^\beta} \right]$$

$$+ \quad \sum_{i^\alpha} (pq|i^\alpha i^\alpha)^b$$

$$+ \quad Q^{\alpha\,(b)}_{pq} \tag{4.23}$$

$$\begin{aligned}
\frac{\partial F^\alpha_{pq}}{\partial R_b} &= \sum_r U^{\alpha b}_{rp} F^\alpha_{rq} \\
&+ \sum_r U^{\alpha b}_{rq} F^\alpha_{pr} \\
&+ H^{\alpha\,(b)}_{pq} \\
&+ \sum_{r^\alpha i^\alpha} U^{\alpha b}_{r^\alpha i^\alpha} \left[2(pq|r^\alpha i^\alpha) + G^{\alpha\alpha}_{pqr^\alpha i^\alpha} \right] \\
&+ \sum_{r^\beta i^\beta} U^{\beta b}_{r^\beta i^\beta} \left[2(pq|r^\beta i^\beta) + G^{\alpha\beta}_{pqr^\beta i^\beta} \right] \\
&+ \sum_{i^\alpha} (pq|i^\alpha i^\alpha)^b \\
&+ Q^{\alpha\,(b)}_{pq} \tag{4.24}
\end{aligned}$$

The derivatives of the orbital energies are the diagonal elements of this expression. Here only the derivatives of the orbital energies of the occupied orbitals are needed, leading to:

$$\begin{aligned}
\frac{\partial F^\alpha_{j^\alpha j^\alpha}}{\partial R_b} &= 2 \sum_r U^{\alpha b}_{rj^\alpha} F^\alpha_{rj^\alpha} \\
&+ H^{\alpha\,(b)}_{j^\alpha j^\alpha} \\
&+ \sum_{ri^\alpha} 2U^{\alpha b}_{ri^\alpha} \left[2(j^\alpha j^\alpha|ri^\alpha) + G^{\alpha\alpha}_{j^\alpha j^\alpha ri^\alpha} \right] \\
&+ \sum_{ri^\beta} U^{\beta b}_{ri^\beta} \left[2(j^\alpha j^\alpha|ri^\beta) + G^{\alpha\beta}_{j^\alpha j^\alpha ri^\beta} \right] \\
&+ \sum_{i^\alpha} (j^\alpha j^\alpha|i^\alpha i^\alpha)^b \\
&+ Q^{\alpha\,(b)}_{j^\alpha j^\alpha} \tag{4.25}
\end{aligned}$$

Using the fact that the orbitals are eigenfunctions of the Fock-matrix and splitting summations over all orbitals into sums over occupied and sums over unoccupied orbitals gives

$$\frac{\partial F^\alpha_{j^\alpha j^\alpha}}{\partial R_b} = -S^{\alpha\,(b)}_{j^\alpha j^\alpha}$$

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$$
\begin{aligned}
+ \quad & H^{\alpha\,(b)}_{j^\alpha j^\alpha} \\
+ \quad & \sum_{k^\alpha i^\alpha} U^{\alpha b}_{k^\alpha i^\alpha} \left[2(j^\alpha j^\alpha | k^\alpha i^\alpha) + G^{\alpha\alpha}_{j^\alpha j^\alpha k^\alpha i^\alpha} \right] \\
+ \quad & \sum_{a^\alpha i^\alpha} U^{\alpha b}_{a^\alpha i^\alpha} \left[2(j^\alpha j^\alpha | a^\alpha i^\alpha) + G^{\alpha\alpha}_{j^\alpha j^\alpha a^\alpha i^\alpha} \right] \\
+ \quad & \sum_{k^\beta i^\beta} U^{\beta b}_{k^\beta i^\beta} \left[2(j^\alpha j^\alpha | k^\beta i^\beta) + G^{\alpha\beta}_{j^\alpha j^\alpha k^\beta i^\beta} \right] \\
+ \quad & \sum_{a^\beta i^\beta} U^{\beta b}_{a^\beta i^\beta} \left[2(j^\alpha j^\alpha | a^\beta i^\beta) + G^{\alpha\beta}_{j^\alpha j^\alpha a^\beta i^\beta} \right] \\
+ \quad & \sum_{i^\alpha} (j^\alpha j^\alpha | i^\alpha i^\alpha)^b \\
+ \quad & Q^{\alpha\,(b)}_{j^\alpha j^\alpha} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (4.26)
\end{aligned}
$$

Using equation (4.12) leads to

$$
\begin{aligned}
\frac{\partial F^\alpha_{\,j^\alpha j^\alpha}}{\partial R_b} \;=\; & -S^{\alpha\,(b)}_{j^\alpha j^\alpha} \epsilon^\alpha_{j^\alpha} \\
+ \quad & H^{\alpha\,(b)}_{j^\alpha j^\alpha} \\
- \quad & \sum_{k^\alpha i^\alpha} S^{\alpha b}_{k^\alpha i^\alpha} \left[(j^\alpha j^\alpha | k^\alpha i^\alpha) + \frac{1}{2} G^{\alpha\alpha}_{j^\alpha j^\alpha k^\alpha i^\alpha} \right] \\
+ \quad & \sum_{a^\alpha i^\alpha} U^{\alpha b}_{a^\alpha i^\alpha} \left[2(j^\alpha j^\alpha | a^\alpha i^\alpha) + G^{\alpha\alpha}_{j^\alpha j^\alpha a^\alpha i^\alpha} \right] \\
- \quad & \sum_{k^\beta i^\beta} S^{\beta b}_{k^\beta i^\beta} \left[(j^\alpha j^\alpha | k^\beta i^\beta) + \frac{1}{2} G^{\alpha\beta}_{j^\alpha j^\alpha k^\beta i^\beta} \right] \\
+ \quad & \sum_{a^\beta i^\beta} U^{\beta b}_{a^\beta i^\beta} \left[2(j^\alpha j^\alpha | a^\beta i^\beta) + G^{\alpha\beta}_{j^\alpha j^\alpha a^\beta i^\beta} \right] \\
+ \quad & \sum_{i^\alpha} (j^\alpha j^\alpha | i^\alpha i^\alpha)^b \\
+ \quad & Q^{\alpha\,(b)}_{j^\alpha j^\alpha} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (4.27)
\end{aligned}
$$

4.5 The 1st derivatives of the orbital coefficients

The derivatives of the unoccupied-occupied block allow the construction of a linear system of equations that determines the response of the orbital coefficients to the perturbation:

$$
\begin{aligned}
\frac{\partial F^\alpha_{\,a^\alpha j^\alpha}}{\partial R_b} \;=\; & \sum_r U^{\alpha b}_{r a^\alpha} F^\alpha_{\,r j^\alpha} \\
+ \quad & \sum_r U^{\alpha b}_{r j^\alpha} F^\alpha_{\,a^\alpha r}
\end{aligned}
$$

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$$+ \quad H^{\alpha\,(b)}_{a^\alpha j^\alpha}$$

$$+ \quad \sum_{r^\alpha i^\alpha} U^{\alpha b}_{r^\alpha i^\alpha} \left[2(a^\alpha j^\alpha | r^\alpha i^\alpha) + G^{\alpha\alpha}_{a^\alpha j^\alpha r^\alpha i^\alpha} \right]$$

$$+ \quad \sum_{r^\beta i^\beta} U^{\beta b}_{r^\beta i^\beta} \left[2(a^\alpha j^\alpha | r^\beta i^\beta) + G^{\alpha\beta}_{a^\alpha j^\alpha r^\beta i^\beta} \right]$$

$$+ \quad \sum_{i^\alpha} (a^\alpha j^\alpha | i^\alpha i^\alpha)^b$$

$$+ \quad Q^{\alpha\,(b)}_{a^\alpha j^\alpha} \tag{4.28}$$

Splitting the sums over all orbitals into sums over occupied and sums over unoccupied orbitals gives

$$\frac{\partial F^\alpha{}_{a^\alpha j^\alpha}}{\partial R_b} \quad = \quad \sum_{i^\alpha} U^{\alpha b}_{i^\alpha a^\alpha} F^\alpha{}_{i^\alpha j^\alpha}$$

$$+ \quad \sum_{b^\alpha} U^{\alpha b}_{b^\alpha j^\alpha} F^\alpha{}_{a^\alpha b^\alpha}$$

$$+ \quad H^{\alpha\,(b)}_{a^\alpha j^\alpha}$$

$$+ \quad \sum_{k^\alpha i^\alpha} U^{\alpha b}_{k^\alpha i^\alpha} \left[2(a^\alpha j^\alpha | k^\alpha i^\alpha) + G^{\alpha\alpha}_{a^\alpha j^\alpha k^\alpha i^\alpha} \right]$$

$$+ \quad \sum_{b^\alpha i^\alpha} U^{\alpha b}_{b^\alpha i^\alpha} \left[2(a^\alpha j^\alpha | b^\alpha i^\alpha) + G^{\alpha\alpha}_{a^\alpha j^\alpha b^\alpha i^\alpha} \right]$$

$$+ \quad \sum_{k^\beta i^\beta} U^{\beta b}_{k^\beta i^\beta} \left[2(a^\alpha j^\alpha | k^\beta i^\beta) + G^{\alpha\beta}_{a^\alpha j^\alpha k^\beta i^\beta} \right]$$

$$+ \quad \sum_{b^\beta i^\beta} U^{\beta b}_{b^\beta i^\beta} \left[2(a^\alpha j^\alpha | b^\beta i^\beta) + G^{\alpha\beta}_{a^\alpha j^\alpha b^\beta i^\beta} \right]$$

$$+ \quad \sum_{i^\alpha} (a^\alpha j^\alpha | i^\alpha i^\alpha)^b$$

$$+ \quad Q^{\alpha\,(b)}_{a^\alpha j^\alpha} \tag{4.29}$$

Using equation (4.12) to eliminate the occupied-occupied blocks of the U-matrix yields

$$\frac{\partial F^\alpha{}_{a^\alpha j^\alpha}}{\partial R_b} \quad = \quad \sum_{i^\alpha} (-U^{\alpha b}_{a^\alpha i^\alpha} - S^{\alpha\,(b)}_{a^\alpha i^\alpha}) F^\alpha{}_{i^\alpha j^\alpha}$$

$$+ \quad \sum_{b^\alpha} U^{\alpha b}_{b^\alpha j^\alpha} F^\alpha{}_{a^\alpha b^\alpha}$$

$$+ \quad H^{\alpha\,(b)}_{a^\alpha j^\alpha}$$

$$- \quad \sum_{k^\alpha i^\alpha} S^{\alpha\,(b)}_{k^\alpha i^\alpha} \left[(a^\alpha j^\alpha | k^\alpha i^\alpha) + \frac{1}{2} G^{\alpha\alpha}_{a^\alpha j^\alpha k^\alpha i^\alpha} \right]$$

$$+ \quad \sum_{b^\alpha i^\alpha} U^{\alpha b}_{b^\alpha i^\alpha} \left[2(a^\alpha j^\alpha | b^\alpha i^\alpha) + G^{\alpha\alpha}_{a^\alpha j^\alpha b^\alpha i^\alpha} \right]$$

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$$
- \sum_{k^\beta i^\beta} S^{\beta\,(b)}_{k^\beta i^\beta} \left[(a^\alpha j^\alpha | k^\beta i^\beta) + \frac{1}{2} G^{\alpha\beta}_{a^\alpha j^\alpha k^\beta i^\beta} \right]
$$

$$
+ \sum_{b^\beta i^\beta} U^{\beta b}_{b^\beta i^\beta} \left[2(a^\alpha j^\alpha | b^\beta i^\beta) + G^{\alpha\beta}_{a^\alpha j^\alpha b^\beta i^\beta} \right]
$$

$$
+ \sum_{i^\alpha} (a^\alpha j^\alpha | i^\alpha i^\alpha)^b
$$

$$
+ \; Q^{\alpha\,(b)}_{a^\alpha j^\alpha} \tag{4.30}
$$

Given that the Fock-matrix is diagonal and using the definition (2.22) of the Fock-matrix together with equation (4.20) yields

$$
\begin{aligned}
\frac{\partial F^\alpha_{a^\alpha j^\alpha}}{\partial R_b} &= \sum_{b^\alpha i^\alpha} [(\epsilon^\alpha_{b^\alpha} - \epsilon^\alpha_{i^\alpha}) \delta_{i^\alpha j^\alpha} \delta_{a^\alpha b^\alpha} + 2(a^\alpha j^\alpha | b^\alpha i^\alpha) + G^{\alpha\alpha}_{a^\alpha j^\alpha b^\alpha i^\alpha}] U^{\alpha b}_{b^\alpha i^\alpha} \\
&+ \sum_{b^\beta i^\beta} U^{\beta b}_{b^\beta i^\beta} \left[2(a^\alpha j^\alpha | b^\beta i^\beta) + G^{\alpha\beta}_{a^\alpha j^\alpha b^\beta i^\beta} \right] \\
&- \sum_{b^\alpha i^\alpha} S^{\alpha\,(b)}_{b^\alpha i^\alpha} \epsilon^\alpha_{i^\alpha} \delta_{i^\alpha j^\alpha} \delta_{a^\alpha b^\alpha} \\
&- \sum_{k^\alpha i^\alpha} S^{\alpha\,(b)}_{k^\alpha i^\alpha} \left[(a^\alpha j^\alpha | k^\alpha i^\alpha) + \frac{1}{2} G^{\alpha\alpha}_{a^\alpha j^\alpha k^\alpha i^\alpha} \right] \\
&- \sum_{k^\beta i^\beta} S^{\beta\,(b)}_{k^\beta i^\beta} \left[(a^\alpha j^\alpha | k^\beta i^\beta) + \frac{1}{2} G^{\alpha\beta}_{a^\alpha j^\alpha k^\beta i^\beta} \right] \\
&+ \; F^{\alpha\,(b)}_{a^\alpha j^\alpha} \tag{4.31}
\end{aligned}
$$

From the Brillouin condition we have that expression (4.31) should equal 0. This gives us a system of simultaneous equations for U_{aj} called the Coupled Perturbed Hartree Fock (CPHF) equations. Essentially equation (4.31) gives the residue of the system of simultaneous equations. Traditionally the terms involving U_{aj} would be considered the left-hand-side, whereas the other terms would be considered the right-hand-side.

In practice what we need is the residue for a given approximation to U. The residue can be used to update U and compute a new residue until convergence is achieved. For this purpose we need to compute the following in the DFT code

$$
\begin{aligned}
G^{\alpha[b]}_{a^\alpha j^\alpha} \\
&= \sum_{b^\alpha i^\alpha} G^{\alpha\alpha}_{a^\alpha j^\alpha b^\alpha i^\alpha} U^{\alpha b}_{b^\alpha i^\alpha} - \sum_{k^\alpha i^\alpha} \frac{1}{2} G^{\alpha\alpha}_{a^\alpha j^\alpha k^\alpha i^\alpha} S^{\alpha\,(b)}_{k^\alpha i^\alpha} \\
&+ \sum_{b^\beta i^\beta} G^{\alpha\beta}_{a^\alpha j^\alpha b^\beta i^\beta} U^{\beta b}_{b^\beta i^\beta} - \sum_{k^\beta i^\beta} \frac{1}{2} G^{\alpha\beta}_{a^\alpha j^\alpha k^\beta i^\beta} S^{\beta\,(b)}_{k^\beta i^\beta} \tag{4.32} \\
&= \sum_{r^\alpha i^\alpha} G^{\alpha\alpha}_{a^\alpha j^\alpha r^\alpha i^\alpha} U^{\alpha b}_{r^\alpha i^\alpha} \\
&+ \sum_{r^\beta i^\beta} G^{\alpha\beta}_{a^\alpha j^\alpha r^\beta i^\beta} U^{\beta b}_{r^\beta i^\beta} \tag{4.33}
\end{aligned}
$$

Substituting the definitions given in equations (4.21) and (4.22) for the G's we have

$$G^{\alpha[b]}_{a^\alpha j^\alpha}$$

$$= \sum_{r^\alpha i^\alpha} \sum_{\mu\nu\lambda\sigma} C^\alpha_{\mu a^\alpha} C^\alpha_{\nu j^\alpha} (C^\alpha_{\lambda r^\alpha} C^\alpha_{\sigma i^\alpha} + C^\alpha_{\lambda i^\alpha} C^\alpha_{\sigma r^\alpha}) \frac{\partial^2 E_{xc}(P^\alpha, P^\beta)}{\partial P^\alpha_{\mu\nu} \partial P^\alpha_{\lambda\sigma}} U^{\alpha b}_{r^\alpha i^\alpha}$$

$$+ \sum_{r^\beta i^\beta} \sum_{\mu\nu\lambda\sigma} C^\alpha_{\mu a^\alpha} C^\alpha_{\nu j^\alpha} (C^\beta_{\lambda r^\beta} C^\beta_{\sigma i^\beta} + C^\beta_{\lambda i^\beta} C^\beta_{\sigma r^\beta}) \frac{\partial^2 E_{xc}(P^\alpha, P^\beta)}{\partial P^\alpha_{\mu\nu} \partial P^\beta_{\lambda\sigma}} U^{\beta b}_{r^\beta i^\beta} \quad (4.34)$$

Using the definition of U we have

$$G^{\alpha[b]}_{a^\alpha j^\alpha}$$

$$= \sum_{\mu\nu\lambda\sigma} C^\alpha_{\mu a^\alpha} C^\alpha_{\nu j^\alpha} \frac{\partial^2 E_{xc}(P^\alpha, P^\beta)}{\partial P^\alpha_{\mu\nu} \partial P^\alpha_{\lambda\sigma}} P^{\alpha b}_{\lambda\sigma}$$

$$+ \sum_{\mu\nu\lambda\sigma} C^\alpha_{\mu a^\alpha} C^\alpha_{\nu j^\alpha} \frac{\partial^2 E_{xc}(P^\alpha, P^\beta)}{\partial P^\alpha_{\mu\nu} \partial P^\beta_{\lambda\sigma}} P^{\beta b}_{\lambda\sigma} \quad (4.35)$$

$$= \sum_{\mu\nu} C^\alpha_{\mu a^\alpha} C^\alpha_{\nu j^\alpha} G^{\alpha[b]}_{\mu\nu} \quad (4.36)$$

where

$$P^{\alpha b}_{\lambda\sigma} = \sum_{r^\alpha i^\alpha} (C^\alpha_{\lambda r^\alpha} C^\alpha_{\sigma i^\alpha} + C^\alpha_{\lambda i^\alpha} C^\alpha_{\sigma r^\alpha}) U^{\alpha b}_{r^\alpha i^\alpha} \quad (4.37)$$

$$P^{\beta b}_{\lambda\sigma} = \sum_{r^\beta i^\beta} (C^\beta_{\lambda r^\beta} C^\beta_{\sigma i^\beta} + C^\beta_{\lambda i^\beta} C^\beta_{\sigma r^\beta}) U^{\beta b}_{r^\beta i^\beta} \quad (4.38)$$

$$G^{\alpha[b]}_{\mu\nu} = \sum_{\lambda\sigma} \frac{\partial^2 E_{xc}(P^\alpha, P^\beta)}{\partial P^\alpha_{\mu\nu} \partial P^\alpha_{\lambda\sigma}} P^{\alpha b}_{\lambda\sigma}$$

$$+ \sum_{\lambda\sigma} \frac{\partial^2 E_{xc}(P^\alpha, P^\beta)}{\partial P^\alpha_{\mu\nu} \partial P^\beta_{\lambda\sigma}} P^{\beta b}_{\lambda\sigma} \quad (4.39)$$

Using the definition for the matrix elements we have that

$$G^{\alpha[b]}_{\mu\nu} = \int (\sum_\zeta [\frac{\partial^2 f}{\partial\zeta\partial\rho_\alpha} \chi_\mu\chi_\nu$$

$$+ \{2\frac{\partial^2 f}{\partial\zeta\partial\gamma_{\alpha\alpha}} \nabla\rho_\alpha + \frac{\partial^2 f}{\partial\zeta\partial\gamma_{\alpha\beta}} \nabla\rho_\beta\} \cdot \nabla(\chi_\mu\chi_\nu)]\zeta^{[b]}$$

$$+ \{2\frac{\partial f}{\partial\gamma_{\alpha\alpha}} \nabla\rho^{[b]}_\alpha + \frac{\partial f}{\partial\gamma_{\alpha\beta}} \nabla\rho^{[b]}_\beta\} \cdot \nabla(\chi_\mu\chi_\nu))dr \quad (4.40)$$

where ζ loops over ρ_α, ρ_β, $\gamma_{\alpha\alpha}$, $\gamma_{\alpha\beta}$ and $\gamma_{\beta\beta}$. The various quantities $\zeta^{[b]}$ are given by

$$\rho^{[b]}_\alpha = \sum_{\mu\nu} P^{\alpha b}_{\mu\nu} \chi_\mu\chi_\nu \quad (4.41)$$

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$$\rho_\beta^{[b]} = \sum_{\mu\nu} P_{\mu\nu}^{\beta b} \chi_\mu \chi_\nu \tag{4.42}$$

$$\nabla\rho_\alpha^{[b]} = \sum_{\mu\nu} P_{\mu\nu}^{\alpha b} \nabla(\chi_\mu \chi_\nu) \tag{4.43}$$

$$\nabla\rho_\beta^{[b]} = \sum_{\mu\nu} P_{\mu\nu}^{\beta b} \nabla(\chi_\mu \chi_\nu) \tag{4.44}$$

$$\gamma_{\alpha\alpha}^{[b]} = 2\nabla\rho_\alpha \cdot \nabla\rho_\alpha^{[b]} \tag{4.45}$$

$$\gamma_{\alpha\beta}^{[b]} = \nabla\rho_\alpha^{[b]} \cdot \nabla\rho_\beta + \nabla\rho_\alpha \cdot \nabla\rho_\beta^{[b]} \tag{4.46}$$

$$\gamma_{\beta\beta}^{[b]} = 2\nabla\rho_\beta \cdot \nabla\rho_\beta^{[b]} \tag{4.47}$$

This concludes the material we need for the "left-hand-side".

The "right-hand-side" includes $Q^{\alpha(b)}_{a^\alpha j^\alpha}$, and involves the Kohn-Sham matrix elements. Taking the explicit derivative of the matrix element contributions will introduce the gradients of the quadrature somewhere. So we need to take a closer look at what that involves:

$$Q^{\alpha(b)}_{a^\alpha j^\alpha} = \sum_{\mu\nu} C^\alpha_{\mu a^\alpha} C^\alpha_{\nu j^\alpha} \frac{\partial E_{xc}^{(b)}(P^\alpha, P^\beta)}{\partial P_{\mu\nu}^\alpha} \tag{4.48}$$

$$= \sum_{\mu\nu} C^\alpha_{\mu a^\alpha} C^\alpha_{\nu j^\alpha} Q^{\alpha(b)}_{\mu\nu} \tag{4.49}$$

where

$$Q^{\alpha(b)}_{\mu\nu} = \frac{\partial E_{xc}^{(b)}(P^\alpha, P^\beta)}{\partial P_{\mu\nu}^\alpha} \tag{4.50}$$

Using the expression for the matrix elements leads to

$$
\begin{aligned}
Q^{\alpha(b)}_{\mu\nu} = {} & \sum_{Ai} w_{Ai} \frac{\partial P_A(r_{Ai})}{\partial R_b} Q^\alpha_{\mu\nu} \\
& + \int \Big(\sum_\zeta \big[\frac{\partial^2 f}{\partial\zeta\partial\rho_\alpha} \chi_\mu\chi_\nu \\
& + \{ 2\frac{\partial^2 f}{\partial\zeta\partial\gamma_{\alpha\alpha}} \nabla\rho_\alpha + \frac{\partial^2 f}{\partial\zeta\partial\gamma_{\alpha\beta}} \nabla\rho_\beta \} \cdot \nabla(\chi_\mu\chi_\nu) \big] \zeta^{(b)} \\
& + \{ 2\frac{\partial f}{\partial\gamma_{\alpha\alpha}} \nabla\rho_\alpha^{(b)} + \frac{\partial f}{\partial\gamma_{\alpha\beta}} \nabla\rho_\beta^{(b)} \} \cdot \nabla(\chi_\mu\chi_\nu) \\
& + \frac{\partial f}{\partial\rho_\alpha} (\chi_\mu\chi_\nu)^b \\
& + \{ 2\frac{\partial f}{\partial\gamma_{\alpha\alpha}} \nabla\rho_\alpha + \frac{\partial f}{\partial\gamma_{\alpha\beta}} \nabla\rho_\beta \} \cdot \nabla(\chi_\mu\chi_\nu)^b \Big) dr
\end{aligned}
\tag{4.51}
$$

where (taking into account that the grid points also depend on the atom posi-

tions)

$$\rho_\alpha(r_{Ai}) = \sum_{B,C} \sum_{\substack{\mu \in \mu_B \\ \nu \in \nu_C}} P_{\mu\nu}^\alpha \chi_\mu(R_B, r_{Ai}) \chi_\nu(R_C, r_{Ai}) \tag{4.52}$$

$$\rho_\alpha^{(d)}(r_{Ai}) = \sum_{B,C} \sum_{\substack{\mu \in \mu_B \\ \nu \in \nu_C}} P_{\mu\nu}^\alpha \frac{\partial\left(\chi_\mu(R_B, r_{Ai})\chi_\nu(R_C, r_{Ai})\right)}{\partial R_D} \tag{4.53}$$

$$\tag{4.54}$$

Depending on which coordinates correspond to that of atom with respect to which we take the derivatives we obtain different expressions

$$\rho_\alpha^{(d)}(r_{Ai}) = \begin{cases} \displaystyle\sum_C \sum_{\substack{\mu \in \mu_D \\ \nu \in \nu_C}} P_{\mu\nu}^\alpha \frac{\partial\chi_\mu(R_D, r_{Ai})}{\partial R_D}\chi_\nu(R_C, r_{Ai}), & B = D \\[2em] \displaystyle\sum_B \sum_{\substack{\mu \in \mu_B \\ \nu \in \nu_D}} P_{\mu\nu}^\alpha \chi_\mu(R_B, r_{Ai})\frac{\partial\chi_\nu(R_D, r_{Ai})}{\partial R_D}, & C = D \\[2em] \displaystyle\sum_{B,C} \sum_{\substack{\mu \in \mu_B \\ \nu \in \nu_C}} P_{\mu\nu}^\alpha \left(\frac{\partial\chi_\mu(R_B, r_{Di})}{\partial R_D}\chi_\nu(R_C, r_{Di}) + \right. & \\[1em] \qquad\qquad \left. \chi_\mu(R_B, r_{Di})\frac{\partial\chi_\nu(R_C, r_{Di})}{\partial R_D}\right) & A = D \\[1em] 0, & A = B = D \\ 0, & A = C = D \end{cases} \tag{4.55}$$

A similar result is obtained for the gradients of the density

$$\nabla\rho_\alpha(r_{Ai}) = \sum_{B,C} \sum_{\substack{\mu \in \mu_B \\ \nu \in \nu_C}} P_{\mu\nu}^\alpha \nabla\left(\chi_\mu(R_B, r_{Ai})\chi_\nu(R_C, r_{Ai})\right) \tag{4.56}$$

$$\nabla\rho_\alpha^{(d)}(r_{Ai}) = \sum_{B,C} \sum_{\substack{\mu \in \mu_B \\ \nu \in \nu_C}} P_{\mu\nu}^\alpha \frac{\partial\nabla\left(\chi_\mu(R_B, r_{Ai})\chi_\nu(R_C, r_{Ai})\right)}{\partial R_D} \tag{4.57}$$

$$\tag{4.58}$$

where the gradient operator works on the coordinates of grid points only. Writ-

ing out we have

$$\nabla\rho_\alpha^{(d)}(r_{Ai}) \;=\; \begin{cases} \displaystyle\sum_C \sum_{\substack{\mu\,\in\,\mu_D \\ \nu\,\in\,\nu_C}} P_{\mu\nu}^\alpha \;\left(\frac{\partial\nabla\chi_\mu(R_D,r_{Ai})}{\partial R_D}\chi_\nu(R_C,r_{Ai}) + \right. & \\ \qquad\qquad\qquad\qquad \left.\frac{\partial\chi_\mu(R_D,r_{Ai})}{\partial R_D}\nabla\chi_\nu(R_C,r_{Ai})\right) & ,\qquad B=D \\[2ex] \displaystyle\sum_B \sum_{\substack{\mu\,\in\,\mu_B \\ \nu\,\in\,\nu_D}} P_{\mu\nu}^\alpha \;\left(\nabla\chi_\mu(R_B,r_{Ai})\frac{\partial\chi_\nu(R_D,r_{Ai})}{\partial R_D} + \right. & \\ \qquad\qquad\qquad\qquad \left.\chi_\mu(R_B,r_{Ai})\frac{\partial\nabla\chi_\nu(R_D,r_{Ai})}{\partial R_D}\right) & ,\qquad C=D \\[2ex] \displaystyle\sum_{B,C} \sum_{\substack{\mu\,\in\,\mu_B \\ \nu\,\in\,\nu_C}} P_{\mu\nu}^\alpha \;\left(\frac{\partial\nabla\chi_\mu(R_B,r_{Di})}{\partial R_D}\chi_\nu(R_C,r_{Di}) + \right. & \\ \qquad\qquad\qquad\qquad \frac{\partial\chi_\mu(R_B,r_{Di})}{\partial R_D}\nabla\chi_\nu(R_C,r_{Di}) & \\ \qquad\qquad\qquad\qquad \nabla\chi_\mu(R_B,r_{Di})\frac{\partial\chi_\nu(R_C,r_{Di})}{\partial R_D} & \\ \qquad\qquad\qquad\qquad \left.\chi_\mu(R_B,r_{Di})\frac{\partial\nabla\chi_\nu(R_C,r_{Di})}{\partial R_D}\right) & ,\qquad A=D \\[2ex] 0, & A=B=D \\[1ex] 0, & A=C=D \end{cases} \tag{4.59}$$

This concludes the derivation of the ingredients needed to construct the linear system of equations for the unoccupied-occupied block of the U-matrix.

Chapter 5

Derivatives and quadratures

5.1 The exchange-correlation energy

The exchange-correlation energy in DFT is defined as

$$E_{xc} = \int f(\rho(R,r))dr \tag{5.1}$$

$$\approx \sum_{Bi} w_{Bi} f(\rho(R, r_{Bi})) \tag{5.2}$$

where we have introduced a quadrature because the function f cannot be integrated analytically. Furthermore, the vector R specifies the locations of the nuclei and r specifies a point in space. To complete the definition we write the density ρ as

$$\rho(R,r) = \sum_i \phi_i^*(R,r)\phi_i(R,r) \tag{5.3}$$

$$\phi_i(R,r) = \sum_j c_{ij} \chi_j(R_j, r) \tag{5.4}$$

which gives the density in terms of the AO-basis as

$$\rho(R,r) = \sum_{ijk} c_{ij}^* c_{ik} \chi_j^*(R_j, r) \chi_k(R_k, r) \tag{5.5}$$

5.2 The exchange-correlation energy gradient

In this document we will consider calculating the gradient (and hessian) of the exchange-correlation energy with respect to nuclear displacements. Also we will take a closer look at the consequences for the gradient expression of introducing a quadrature to evaluate the energy. Essentially the quadrature leads to two views to calculating the gradient.

The first view is to take the integral expression for the exchange-correlation energy (5.1) and differentiate it

$$\nabla_A E_{xc} \;=\; \int \nabla_A f(\rho(R,r))dr \tag{5.6}$$

where ∇_A denotes the fact that we are taking the gradient with respect to nuclear displacements of atom A. Just as we cannot integrate $f(\rho(R,r))$ analytically, we also cannot integrate $\nabla_A f(\rho(R,r))$ analytically and we have to rely on a numerical integration

$$\nabla_A E_{xc} \;\approx\; \sum_{Bi} w_{Bi} \, \nabla_A f(\rho(R,r))|_{r=r_{Bi}} \tag{5.7}$$

Essentially this approach is equivalent to applying the Hellman-Feynman theorem. Writing this expression out in more detail we have

$$\nabla_A E_{xc} \;\approx\; \sum_{Bi} w_{Bi} \left.\frac{\partial f(\rho)}{\partial \rho}\right|_{\rho=\rho(R,r_{Bi})} \cdot \left.\frac{\mathrm{d}\rho(R,r)}{\mathrm{d}R}\right|_{R=R,r=r_{Bi}} \nabla_A R \tag{5.8}$$

Note that here the contributions from $\nabla_A r$ are zero because the quadrature was introduced only after differentiation.

The second approach starts with the fact that the energy expression we are actually using involves a quadrature, i.e.

$$E_{xc} \;\approx\; \sum_{Ai} w_{Ai} f(\rho(R,r_{Ai})) \tag{5.9}$$

and therefore the gradient of the energy is the gradient of that expression, which yields

$$\nabla_A E_{xc} \;\approx\; \sum_{Bi} \nabla_A w_{Bi} f(\rho(R,r_{Bi})) \tag{5.10}$$

Writing this expression out in more detail leads to the equation

$$\begin{aligned}
\nabla_A E_{xc} \;\approx\; & \sum_{Bi} f(\rho(R,r_{Bi})) \nabla_A w_{Bi} \\
& + \sum_{Bi} w_{Bi} \left.\frac{\partial f(\rho)}{\partial \rho}\right|_{\rho=\rho(R,r_{Bi})} \left.\frac{\mathrm{d}\rho(R,r)}{\mathrm{d}R}\right|_{R=R,r=r_{Bi}} \nabla_A R \\
& + \sum_{Bi} w_{Bi} \left.\frac{\partial f(\rho)}{\partial \rho}\right|_{\rho=\rho(R,r_{Bi})} \left.\frac{\partial \rho(R,r)}{\partial r}\right|_{R=R,r=r_{Bi}} \nabla_A r
\end{aligned} \tag{5.11}$$

In this case we find that we actually have contributions from the gradients of the quadrature weights and the grid points.

Both equations (5.8) and (5.11) yield identical results in the limit of an exact quadrature, but for every other quadrature the results will be different. To illustrate the severity of the difference, we computed the density of a lithium

Table 5.1: A comparison of the analytically computed DFT gradients of LiF (based on the Hellmann-Feynman approach and the full gradient approach) and the numerical gradients where all densities were optimised using an accurate grid

Grid	Hellman-Feynman gradient		Full gradient		Numerical gradient	
	Li (E_H/a_0)	F (E_H/a_0)	Li (E_H/a_0)	F (E_H/a_0)	Li (E_H/a_0)	F (E_H/a_0)
low	-0.0001154	0.0479085	-0.0701652	0.0701652	-0.0721060	0.0721060
medium	-0.0002365	0.0018857	-0.0070063	0.0070063	-0.0069640	0.0069640
high	-0.0000843	-0.0003445	0.0004372	-0.0004372	0.0004380	-0.0004380
veryhigh	-0.0001083	0.0002059	-0.0002052	0.0002052	-0.0002060	0.0002060

All calculations were performed using GAMESS-UK. The LiF bond length was 2.9322936 a_0, with the bond length distorted by $+0.005$ a_0 and -0.005 a_0 for the numerical gradients. The 6-31G* basis set was used with the B3LYP functional. The density was optimised with the veryhigh accuracy grid. The low, medium, high and veryhigh grids used are defined in the GAMESS-UK documentation; in all calculations the Murray, Handy and Laming weighting scheme was used instead of the default.

fluoride molecule with a high accuracy grid, and then computed the gradients with various grid sizes once with equation (5.8) and once with equation (5.11). The results are given in table 5.1. From this table we can learn two things.

First, for heteronuclear molecules the quadrature gradient contributions can be essential to maintain the translational invariance of the energy. This translational invariance requires that the gradients along 1 coordinate of all atoms add up to zero. Clearly this is not the case with the Hellman-Feynman gradients, but the full gradient is correct in this respect.

Second, including the quadrature gradient terms does not necessarily lead to more accurate gradients. Assuming that the full gradient results with the veryhigh grid are the exact values, it is clear that the full gradient results with the low grid exhibit far greater errors than the Hellman-Feynman gradient with the low grid.

The conclusion is that the question as to whether the quadrature gradient terms should be included is a consistency matter. In cases such as dynamics, where it is essential that the energy and the gradient are consistent, using the full gradient expression is compulsory. In simple searches for local minima of the energy (e.g. steepest descent), the Hellman-Feynman gradient may be sufficient. Moreover, if one decides to use the full gradient expression, then one should be aware that this makes sense only if the grid with which the density is optimised is identical to the grid used to evaluate the gradient, otherwise consistency between the energy and the gradient will be lost.

5.3 Definition of the quadrature

In the case where we use a quadrature we follow Becke's scheme [2] where the total grid is constructed from atomic grids merged together through a weighting

scheme (see appendix A). There are two ways to approach this quadrature that lead to equivalent results but different gradient expressions. The view adopted by B.G. Johnson et al. [6] is essentially that one chooses a quadrature point $r_i = r$ in space independent of the location of the atoms and then assigns it to an atom to define its atomic weight $w'_i = w'(R_B, r)$. The atomic weight in this case is a function of the location of the atom. The approach adopted by J. Tozer is that each quadrature point is defined relative to some atom $r_i = R_B + r$. The atomic weight in this case is $w'_i = w'(r)$ and is independent of location of the atom.

The approach adopted by Tozer is probably the most consistent and can be used to derive both gradient and hessian equations. The approach adopted by Johnson on the face of it involves much more complicated terms in calculating the gradient, e.g. $dw'(R_B, r)/dR_B$, although in practice all these terms can be avoided using the translational invariance of the energy. In that case the equations become simpler than following Tozer. The problem is that it is conceptually much more complicated to use Johnson's approach to calculate hessians.

5.4 Johnson's formulation of the weighting scheme and the gradient of the weights

As indicated above Johnson considers a grid point as being independent of the molecular geometry. The consequence is that the atomic weight becomes a function of the location of the atom. The weighting in this formulation becomes

$$w_B(R,r) = w'(R_B, r)\frac{P_B(R,r)}{Z(R,r)} \tag{5.12}$$

$$Z(R,r) = \sum_C P_C(R,r) \tag{5.13}$$

$$P_B(R,r) = \prod_{C \neq B} s(\nu(R_{\text{Bragg}}, B, C, \mu(R_B, R_C, r))) \tag{5.14}$$

$$\mu(R_B, R_C, r) = \frac{|r - R_B| - |r - R_C|}{|R_B - R_C|} \tag{5.15}$$

$$\tag{5.16}$$

where r is the fixed grid point; the cut-off profile function s and the boundary shifting function ν have been defined by Becke [2].

In calculating the gradients of the weights the most complicated term comes from $\nabla_B w'(R_B, r)$. In practice evaluating this term can be circumvented using the translational variance of the energy, i.e.

$$\nabla_B w_B(R,r) = -\sum_{A \neq B} \nabla_A w_B(R,r) \tag{5.17}$$

so the only gradients we need are of the form $\nabla_A w_B(R, r)$, where we have the weights of grid points relative to atom B differentiated with respect to nuclear displacements of all other atoms. Writing this expression out gives

$$\nabla_A w_B(R, r) = w'(R_B, r)\left[\frac{\nabla_A P_B(R, r)}{Z(R, r)} - P_B(R, r)\frac{\nabla_A Z(R, r)}{Z^2(R, r)}\right] \quad (5.18)$$

where $A \neq B$. The first term can be written out as

$$\nabla_A P_B(R, r) = \nabla_A \prod_{C \neq B} s(R_B, R_C, r) \quad (5.19)$$

$$= \frac{P_B(R, r)}{s(R_B, R_A, r)}\nabla_A s(R_B, R_A, r) \quad (5.20)$$

The second term becomes

$$\nabla_A Z(R, r) = \nabla_A \sum_B P_B(R, r) \quad (5.21)$$

$$= \nabla_A \sum_B \prod_{C \neq B} s(R_B, R_C, r) \quad (5.22)$$

$$= \sum_{C \neq A} \frac{P_A(R, r)}{s(R_A, R_C, r)}\nabla_A s(R_A, R_C, r)$$

$$+ \sum_{B \neq A} \frac{P_B(R, r)}{s(R_B, R_A, r)}\nabla_A s(R_B, R_A, r) \quad (5.23)$$

The cut-off profiles s are functions of ν which is in turn a function of the Bragg-Slater radii of the atoms involved and the elliptical coordinate μ

$$s(R_B, R_C, r) = s(\nu(R_{\text{Bragg}}, \mu(R_B, R_C, r))) \quad (5.24)$$

The gradient of this becomes

$$\nabla_A s(R_B, R_C, r) = \left.\frac{ds(\nu)}{d\nu}\right|_{\nu=\nu(R_{\text{Bragg}}, \mu(R_B, R_C, r))}$$

$$\cdot \left.\frac{d\nu(R_{\text{Bragg}}, \mu)}{d\mu}\right|_{\mu=\mu(R_B, R_C, r)}$$

$$\cdot \nabla_A \mu(R_B, R_C, r) \quad (5.25)$$

$$\nabla_A \mu(R_A, R_C, r) = \frac{X_A - x}{|r - R_A||R_A - R_C|}$$

$$+ \frac{(|r - R_A| - |r - R_C|)(X_C - X_A)}{|R_A - R_C|^3} \quad (5.26)$$

$$\nabla_A \mu(R_B, R_A, r) = \frac{x - X_A}{|r - R_A||R_B - R_A|}$$

$$+ \frac{(|r - R_B| - |r - R_A|)(X_B - X_A)}{|R_B - R_A|^3} \quad (5.27)$$

which completes the gradient expression.

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5.5 Tozer's formulation of the weighting scheme and the gradient of the weights

According to Tozer, the location of the quadrature point is a function of the location of the atom to which it belongs. The atomic weight in this is case is dependent only on the relative position of the grid point to the atom and therefore is independent of the geometry. This view point leads to defining the weighting scheme as

$$w_B(R, r_B) = w'(r) \frac{P_B(R, r_B)}{Z(R, r_B)} \tag{5.28}$$

$$Z(R, r_D) = \sum_C P_C(R, r_D) \tag{5.29}$$

$$P_B(R, r_D) = \prod_{C \neq B} s(\nu(R_{\text{Bragg}}, B, C, \mu(R_B, R_C, r_D))) \tag{5.30}$$

$$\mu(R_B, R_C, r_D) = \frac{|r_D - R_B| - |r_D - R_C|}{|R_B - R_C|} \tag{5.31}$$

$$r_D = R_D + r \tag{5.32}$$

where $w'(r)$ is the weight in the atomic grid, and r gives the coordinates of the point assuming the atom is located at the origin.

The gradient of the weights now becomes

$$\nabla_A w_B(R, r_B) = w'(r) \left[\frac{\nabla_A P_B(R, r_B)}{Z(R, r_B)} - P_B(R, r_B) \frac{\nabla_A Z(R, r_B)}{Z^2(R, r_B)} \right] \tag{5.33}$$

where there is no restriction on A. The first term can be written as

$$\nabla_A P_B(R, r_B) = \nabla_A \prod_{C \neq B} s(R_B, R_C, r_B) \tag{5.34}$$

$$= \sum_{C \neq A} \frac{P_A(R, r_A)}{s(R_A, R_C, r_A)} \nabla_A s(R_A, R_C, r_A)$$

$$+ \frac{P_B(R, r_B)}{s(R_B, R_A, r_B)} \nabla_A s(R_B, R_A, r_B) \tag{5.35}$$

The second term becomes

$$\nabla_A Z(R, r_D) = \nabla_A \sum_B P_B(R, r_D) \tag{5.36}$$

$$= \nabla_A \sum_B \prod_{C \neq B} s(R_B, R_C, r_D) \tag{5.37}$$

$$= \sum_{C \neq A} \frac{P_A(R, r_D)}{s(R_A, R_C, r_D)} \nabla_A s(R_A, R_C, r_D)$$

$$+ \sum_{B \neq A} \frac{P_B(R, r_D)}{s(R_B, R_A, r_D)} \nabla_A s(R_B, R_A, r_D)$$

$$+ \sum_{B,C \neq B} \frac{P_B(R, r_A)}{s(R_B, R_C, r_A)} \nabla_A s(R_B, R_C, r_A) \qquad (5.38)$$

The next step is to consider $\nabla_A s(R_B, R_C, r_D)$ which yields

$$
\begin{aligned}
\nabla_A s(R_B, R_C, r_D) &= \left. \frac{ds(\nu)}{d\nu} \right|_{\nu = \nu(R_{\mathrm{Bragg}}, \mu)} \\
&\quad \cdot \left. \frac{d\nu(\mu)}{d\mu} \right|_{\mu = \mu(R_B, R_C, r_D)} \\
&\quad \cdot \nabla_A \mu(R_B, R_C, r_D) \qquad (5.39)
\end{aligned}
$$

so the all important ingredient is $\nabla_A \mu(R_B, R_C, r_D)$, which yields

$$
\begin{aligned}
\nabla_A \mu(R_A, R_C, r_D) &= \frac{X_A - x_D}{|r_D - R_A||R_A - R_C|} \\
&\quad + \frac{(|r_D - R_A| - |r_D - R_C|)(X_C - X_A)}{|R_A - R_C|^3} \qquad (5.40) \\
\nabla_A \mu(R_B, R_A, r_D) &= \frac{x_D - X_A}{|r_D - R_A||R_B - R_A|} \\
&\quad + \frac{(|r_D - R_B| - |r_D - R_A|)(X_B - X_A)}{|R_B - R_A|^3} \qquad (5.41) \\
\nabla_A \mu(R_B, R_C, r_A) &= \frac{x_D - X_B}{|r_D - R_B||R_B - R_C|} \\
&\quad - \frac{x_D - X_C}{|r_D - R_C||R_B - R_C|} \qquad (5.42)
\end{aligned}
$$

$$(5.43)$$

5.6 The exchange-correlation energy hessian

In this case we will consider the case including the derivatives of the weights only. So we assume that the energy is given by

$$E_{xc} \approx \sum_{Ai} w_{Ai} f(\rho(R, r_{Ai})) \qquad (5.44)$$

and therefore the hessian of the energy is the hessian of that expression which yields

$$\nabla_A \nabla_B E_{xc} \approx \sum_{Bi} \nabla_A \nabla_B w_{Ci} f(\rho(R, r_{Ci})) \qquad (5.45)$$

writing this expression out in more detail leads to the equation

$$\nabla_A \nabla_B E_{xc} \approx \sum_{Ci} [\nabla_A \nabla_B w_{Ci}] f(\rho(R, r_{Ci}))$$

$$+ \sum_{Ci} [\nabla_A w_{Ci}][\nabla_B f(\rho(R, r_{Ci}))]$$

$$+ \sum_{Ci} [\nabla_B w_{Ci}][\nabla_A f(\rho(R, r_{Ci}))]$$

$$+ \sum_{Ci} w_{Ci}[\nabla_A \nabla_B f(\rho(R, r_{Ci}))] \tag{5.46}$$

Obviously the first derivatives of the weights have already been derived, so that only the second derivatives are of interest.

5.7 Johnson's approach applied to the hessian of the weights

We start from the same formulation of the weights as in section 5.4. In calculating the hessians of the weights the two most complicated terms will be $\nabla_A \nabla_B w'(R_B, r)$ and $\nabla_B \nabla_B w'(R_B, r)$. In practice we can use the translational invariance of the energy. This implies that all derivatives of the energy have to be translationally invariant as well. Thus we can use

$$\nabla_A \nabla_B w_B(R, r) = -\sum_{C \neq B} \nabla_A \nabla_C w_B(R, r) \tag{5.47}$$

$$\nabla_B \nabla_B w_B(R, r) = -\sum_{A \neq B} \nabla_A \nabla_B w_B(R, r) \tag{5.48}$$

where the latter equation can be evaluated with help from the first.

Thus the basic building block we need is $\nabla_A \nabla_B w_C(R, r)$ which is

$$\nabla_A \nabla_B w_C(R, r) = w'(R_C, r) \left[\frac{\nabla_A \nabla_B P_C(R, r)}{Z(R, r)} \right.$$
$$- \frac{\{\nabla_A P_C\}\{\nabla_B Z(R, r)\}}{Z^2(R, r)}$$
$$- \frac{\{\nabla_B P_C\}\{\nabla_A Z(R, r)\}}{Z^2(R, r)}$$
$$- \frac{P_C \nabla_A \nabla_B Z(R, r)}{Z^2(R, r)}$$
$$\left. + \frac{2 P_C \nabla_A Z \nabla_B Z}{Z^3(R, r)} \right] \tag{5.49}$$

where

$$\nabla_A P_C(R, r) = \nabla_A \prod_{D \neq C} s(R_C, R_D, r) \tag{5.50}$$

$$= \frac{P_C(R, r)}{s(R_C, R_A, r)} \nabla_A s(R_C, R_A, r) \tag{5.51}$$

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$$\nabla_B P_C(R,r) = \frac{P_C(R,r)}{s(R_C,R_B,r)}\nabla_B s(R_C,R_B,r) \tag{5.52}$$

If $A \neq B \neq C \neq A$ then the 2nd derivative can be written as

$$\nabla_A\nabla_B P_C(R,r) = \frac{P_C(R,r)}{s(R_C,R_A,r)s(R_C,R_B,r)}$$
$$\cdot \; \{\nabla_A s(R_C,R_A,r)\}\{\nabla_B s(R_C,R_B,r)\} \tag{5.53}$$

however in the case that $A = B \neq C$ we have

$$\begin{aligned}
\nabla_A\nabla_A P_C(R,r) &= \frac{P_C(R,r)}{s(R_C,R_A,r)^2}\{\nabla_A s(R_C,R_A,r)\}^2 \\
&- \frac{P_C(R,r)}{s(R_C,R_A,r)^2}\{\nabla_A s(R_C,R_A,r)\}^2 \\
&+ \frac{P_C(R,r)}{s(R_C,R_A,r)}\nabla_A\nabla_A s(R_C,R_A,r) \tag{5.54} \\
&= \frac{P_C(R,r)}{s(R_C,R_A,r)}\nabla_A\nabla_A s(R_C,R_A,r) \tag{5.55}
\end{aligned}$$

Now we need the 2nd derivatives of the cut-off profile

$$\begin{aligned}
\nabla_A\nabla_A s(\nu(\mu(R_C,R_D,r))) &= \frac{d^2 s(\nu)}{d\nu^2}\left[\frac{d\nu}{\mu}\nabla_A\mu(R_C,R_D,r)\right]^2 \\
&+ \frac{ds(\nu)}{d\nu}\frac{d^2\nu}{\mu^2}\left[\nabla_A\mu(R_C,R_D,r)\right]^2 \\
&+ \frac{ds(\nu)}{d\nu}\frac{d\nu}{\mu}\nabla_A\nabla_A\mu(R_C,R_D,r) \tag{5.56}
\end{aligned}$$

The derivatives of μ are

$$\begin{aligned}
\mu(R_C,R_D,r) &= (|r-R_C|-|r-R_D|)\cdot|R_C-R_D|^{-1} \tag{5.57} \\
\frac{d\mu(R_A,R_D,r)}{dX_A} &= -(x-X_A)\cdot|r-R_A|^{-1}\cdot|R_A-R_D|^{-1} \\
&- (X_A-X_D)\cdot(|r-R_A|-|r-R_D|) \\
&\cdot|R_A-R_D|^{-3} \tag{5.58} \\
\frac{d^2\mu(R_A,R_D,r)}{dX_A^2} &= |r-R_A|^{-1}\cdot|R_A-R_D|^{-1} \\
&+ -(x-X_A)^2\cdot|r-R_A|^{-3}\cdot|R_A-R_D|^{-1} \\
&+ 2(x-X_A)(X_A-X_D)\cdot|r-R_A|^{-1}\cdot|R_A-R_D|^{-3} \\
&+ -(|r-R_A|-|r-R_D|)\cdot|R_A-R_D|^{-3} \\
&+ 3(X_A-X_D)^2\cdot(|r-R_A|-|r-R_D|) \\
&\cdot|R_A-R_D|^{-5} \tag{5.59} \\
\frac{d^2\mu(R_A,R_D,r)}{dX_A dY_A} &= -(y-Y_A)(x-X_A)\cdot|r-R_A|^{-3}\cdot|R_A-R_D|^{-1}
\end{aligned}$$

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$$
\begin{aligned}
&+\quad (y - Y_A)(X_A - X_D) \cdot |r - R_A|^{-1} \cdot |R_A - R_D|^{-3} \\
&+\quad (x - X_A)(Y_A - Y_D) \cdot |r - R_A|^{-1} \cdot |R_A - R_D|^{-3} \\
&+\quad 3(X_A - X_D)(Y_A - Y_D) \cdot (|r - R_A| - |r - R_D|) \\
&\qquad \cdot |R_A - R_D|^{-5} \qquad\qquad\qquad (5.60)
\end{aligned}
$$

$$
\begin{aligned}
\frac{\mathrm{d}\mu(R_C, R_A, r)}{\mathrm{d}X_A} &= \quad (x - X_A) \cdot |r - R_A|^{-1} \cdot |R_C - R_A|^{-1} \\
&+\quad (X_C - X_A) \cdot (|r - R_C| - |r - R_A|) \\
&\qquad \cdot |R_C - R_A|^{-3} \qquad\qquad\qquad (5.61)
\end{aligned}
$$

$$
\begin{aligned}
\frac{\mathrm{d}^2\mu(R_C, R_A, r)}{\mathrm{d}X_A^2} &= \quad -|r - R_A|^{-1} \cdot |R_C - R_A|^{-1} \\
&+\quad (x - X_A)^2 \cdot |r - R_A|^{-3} \cdot |R_C - R_A|^{-1} \\
&+\quad 2(x - X_A)(X_C - X_A) \cdot |r - R_A|^{-1} \cdot |R_C - R_A|^{-3} \\
&+\quad -(|r - R_C| - |r - R_A|) \cdot |R_C - R_A|^{-3} \\
&+\quad 3(X_C - X_A)^2 \cdot (|r - R_C| - |r - R_A|) \\
&\qquad \cdot |R_C - R_A|^{-5} \qquad\qquad\qquad (5.62)
\end{aligned}
$$

$$
\begin{aligned}
\frac{\mathrm{d}^2\mu(R_C, R_A, r)}{\mathrm{d}X_A \mathrm{d}Y_A} &= \quad (x - X_A)(y - Y_A) \cdot |r - R_A|^{-3} \cdot |R_C - R_A|^{-1} \\
&+\quad (y - Y_A)(X_C - X_A) \cdot |r - R_A|^{-1} \cdot |R_C - R_A|^{-3} \\
&+\quad (x - X_A)(Y_C - Y_A) \cdot |r - R_A|^{-1} \cdot |R_C - R_A|^{-3} \\
&+\quad 3(X_C - X_A)(Y_C - Y_A) \cdot (|r - R_C| - |r - R_A|) \\
&\qquad \cdot |R_C - R_A|^{-5} \qquad\qquad\qquad (5.63)
\end{aligned}
$$

5.8   Notes

The distance between two points is defined as

$$
\begin{aligned}
|R_A - R_B| &= \quad \left\{ (X_A - X_B)^2 + (Y_A - Y_B)^2 + (Z_A - Z_B)^2 \right\}^{1/2} \\
\frac{\mathrm{d}|R_A - R_B|^n}{\mathrm{d}X_A} &= \quad n \left\{ (X_A - X_B)^2 + (Y_A - Y_B)^2 + (Z_A - Z_B)^2 \right\}^{(n-2)/2} (X_A - X_B) \\
&= \quad n|R_A - R_B|^{n-2}(X_A - X_B) \qquad\qquad\qquad (5.64) \\
\frac{\mathrm{d}|R_A - R_B|^n}{\mathrm{d}X_B} &= \quad -n|R_A - R_B|^{n-2}(X_A - X_B) \qquad\qquad\qquad (5.65) \\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (5.66)
\end{aligned}
$$

Chapter 6

Implementation details

In this chapter we provide an overview of the issues around the implementation of the DFT hessian. This overview also indicates the changes made to the code so that they can be found easily.

6.1 Design considerations

To appreciate the choices made to incorporate the DFT hessians into the existing code, one needs to understand the structure of the original code. GAMESS-UK [3] is a general purpose molecular ab-initio electronic structure code that offers a wide range of functionality. In particular it offers extensive Hartree-Fock type capabilities, including Restricted and Unrestricted Hartree-Fock models (RHF, UHF).

The most widely used DFT model, called the Kohn-Sham model, relies on equations that are only slightly different from the Hartree-Fock models. The quantities needed for the Kohn-Sham model require a substantial amount of code to implement them but the Kohn-Sham equations to be solved can be constructed starting from a Hartree-Fock code with only minor modifications.

In the design phase of the CCP1 DFT module it was realised that the above consideration offered the opportunity to separate most of the DFT code from the main code. The code implementing the Kohn-Sham quantities would be collected in a relatively independent module. This module would be called from the Hartree-Fock programs requiring only a small Application Programmers Interface (API). The resulting interface provide three main capabilities;

- calculating the Kohn-Sham exchange-correlation energy

- calculating the Kohn-Sham matrix elements

- calculating the Kohn-Sham gradient contributions.

The loose coupling between the Hartree-Fock and the DFT code provided the opportunity to distribute the DFT module to the CCP1 community independent

from the main code. Other groups can integrate this DFT code with their own ab-initio programs without too much effort if they wish.

The DFT hessian can be implemented using the same design strategy. The Hartree-Fock code can be modified to include Kohn-Sham contributions to the CPHF equations, and the Hessian expression. These terms were made available to the Hartree-Fock code through two additional API functions. The code to compute these quantities was integrated into the DFT module to guarantee

- optimal code reuse opportunities during the implementation phase,

- consistency of the quadrature through the energy, gradient and hessian calculations, and

- optimal interoperability with other main codes that already use the DFT module

Below the changes involved will be outlined in more detail.

6.2   Additions to the DFT module API

The DFT module API was extended by two functions `CD_cphf` and `CD_hessian`.

The function `CD_cphf` can compute two contributions to the CPHF equations in the AO-basis. The first contribution consists of $Q^{\alpha (b)}_{\mu\nu}$ and $Q^{\beta (b)}_{\mu\nu}$ as defined in equation (4.51). These terms contribute to the right-hand-side of the CPHF equations. The second contribution consists of $G^{\alpha [b]}_{\mu\nu}$ and $G^{\beta [b]}_{\mu\nu}$ as defined in equations (4.40) and (4.39). These terms contribute to the right-hand-side of the CPHF equations. As they again depend on the current guess for the solution they need to be recomputed at every iteration in the linear system solver. However, the choice of passing this quantity between the DFT module and the Hartree-Fock code limits the amount of data being transfered to the minimum. This way memory limitations are pushed back to larger molecules than would otherwise be the case. The computation of each of these contributions can be switched on or off using a boolean argument.

The function `CD_hessian` computes the DFT contributions to the hessian expression. These terms are defined in equations (4.2) and beyond.

6.3   Modifications of the main code

To appreciate the changes required to incorporate the DFT contributions into the second derivatives an overview of the code seems useful. Below an overview of the Hartree-Fock second derivative code within GAMESS-UK is given. To illustrate where the DFT API needs to be called these calls have been included:

```
scf               Hartree-Fock program driver
  rhfclm          Hartree-Fock program
    hstar         Fock matrix builder
```

```
       CD_energy       Kohn-Sham matrix builder
       diis            Fock matrix extrapolation
       jacobi          Diagonalisation
hfgrad
  stvder               1-electron derivative integrals
  jkder                2-electron derivative integrals
     dabab             construction of HF density matrix elements
     CD_cphf           DFT terms added on to derivative Fock matrices
     dgenrl            construction of 2-electron derivative integrals
     fockd2            HF terms added on to derivative Fock matrices
     formeg            adding 2-electron terms onto gradient
chfndr
  chfcls               Construct the HF terms of CPHF matrix
  rhscl                Construct the CPHF right-hand-sides
    chfdftrhs
       CD_cphf         Calculate DFT right-hand-side contributions
  chfdrv
    chfeqv             Solve the CPHF equations
      chfdftau
        CD_cphf        Calculate DFT left-hand-side contributions
dertwo
  chfcla               assemble wavefunction contribution
  dr2nc0               2nd derivative of nuclear contribution
  dr2ovl               2nd derivative of overlap integrals
  dr2ke                2nd derivative of kinetic energy integrals
  dr2pe                2nd derivative of 1-electron potential energy integrals
  dr2dft
    CD_hessian         2nd derivative of DFT contributions
  dr2int               2nd derivative of HF 2-electron integrals
    dr2den             HF density matrix construction
```

To incorporate the DFT contributions correctly into the Hartree-Fock code two types of changes are required.

First, the DFT contributions account for terms due to the exchange-correlation energy replacing the Hartree-Fock exchange terms. Therefore, the Hartree-Fock exchange contributions must be zeroed or in the case of hybrid models be suppressed. For this purpose the exchange integrals were scaled with a Hartree-Fock exchange fraction called hf_wght in:

- subroutine fockd2 scaling down the Hartree-Fock exchange integrals that contribute to $Q^{\alpha(b)}$.

- subroutine dabab scaling down the density matrix terms that are associated with the Hartree-Fock exchange in the gradient.

- subroutine rhscl scaling down the Hartree-Fock exchange integrals that contribute to the right-hand-side, i.e. the Hartree-Fock equivalent of the $\sum_{ki} G^{\alpha\alpha}_{ajki} S^{\alpha(b)}_{ki}$ terms in equation (4.31).

- subroutine `chfcls` scaling down the exchange integrals that contribute to the Hartree-Fock exchange equivalent of the $\sum_{bi} G^{\alpha\alpha}_{ajbi} U^\alpha_{bi}$ terms in the left-hand-side of the CPHF equations.

- subroutine `sgmatm` scaling down the Hartree-Fock exchange integrals that contribute to the gradient of the Fock matrix. I.e. the Hartree-Fock exchange contribution to $F^\alpha{}_{jj}$.

- subroutine `dabab` scaling down the density matrix terms that are associated with the Hartree-Fock exchange in $E^{(a)(b)}$.

The second category of changes involves computation of the DFT contributions and their subsequent addition to the remaining HF terms. In the CPHF equations additional code is needed because the main code works in MO-basis whereas the DFT module works in AO-basis. This interfacing issue was resolved by introducing appropriate wrapper subroutines for the DFT module functions. The changes involved:

- calling `function CD_cphf` from within `subroutine jkder` to calculate $Q^{\alpha(b)}$ for the right-hand-side.

- introducing the `subroutine chfdftrhs` to calculate the $\sum_{ki} G^{\alpha\alpha}_{ajki} S^{\alpha(b)}_{ki}$ terms for the right-hand-side of CPHF equations. This subroutine is called from within `subroutine rhscl`.

- introducing the `subroutine chfdftau` to calculate the $\sum_{bi} G^{\alpha\alpha}_{ajbi} U^\alpha_{bi}$ terms for the left-hand-side of CPHF equations. This subroutine is called from within `subroutine chfeqv`.

- introducing the `subroutine dft_dfock` to calculate the $\sum_{bi} G^{\alpha\alpha}_{ajbi} U^\alpha_{bi}$ contributions to $F^\alpha{}_{jj}$. These contributions can be calculated using `function CD_cphf`. The `subroutine dft_dfock` is called from `subroutine pfockc`.

- introducing the `subroutine dr2dft` that calls `function CD_hessian` to calculate $E^{(a)(b)}$. This subroutine is called from within `subroutine dertwo`.

Chapter 7

Conclusion

This report details the equations required to implement vibrational frequencies within the framework of DFT. Also it outlines the changes required to a Hartree-Fock code to include this functionality. The formalism as presented here has been implemented in the CCP1 DFT module and incorporated into the GAMESS-UK electronic structure code. Work on efficiency enhancements due to various screening techniques and effective parallelisation of the formalism is currently in progress.

Appendix A

Becke weights

In the Becke weighting scheme the function s is defined as

$$s(\nu) = \frac{1}{2}[1 - f(f(f(\nu)))] \tag{A.1}$$

$$f(\nu) = \frac{3}{2}\nu - \frac{1}{2}\nu^3 \tag{A.2}$$

$$\nu(\mu) = \mu + a\left(1 - \mu^2\right) \tag{A.3}$$

For the 1st derivative one obtains

$$\frac{\partial f(\nu)}{\partial \nu} = \frac{3}{2} - \frac{3}{2}\nu^2 \tag{A.4}$$

$$\frac{\partial \nu(\mu)}{\partial \mu} = 1 - 2a\mu \tag{A.5}$$

$$\frac{\partial s(\nu(\mu))}{\partial \mu} = -\frac{1}{2}\frac{\partial f(f(f(\nu(\mu))))}{\partial f(f(\nu(\mu)))} \cdot \frac{\partial f(f(\nu(\mu)))}{\partial f(\nu(\mu))} \cdot \frac{\partial f(\nu(\mu))}{\partial \nu(\mu)} \cdot \frac{\partial \nu(\mu)}{\partial \mu} \tag{A.6}$$

For the 2nd derivative one obtains

$$\frac{\partial^2 f(\nu)}{\partial \nu^2} = -3\nu \tag{A.7}$$

$$\frac{\partial^2 \nu(\mu)}{\partial \mu^2} = -2a \tag{A.8}$$

$$\begin{aligned}\frac{\partial^2 s(\nu(\mu))}{\partial \mu^2} = {} & -\frac{1}{2}\frac{\partial^2 f(f(f(\nu)))}{\partial f(f(\nu))^2} \cdot \left[\frac{\partial f(f(\nu))}{\partial f(\nu)} \cdot \frac{\partial f(\nu)}{\partial \nu} \cdot \frac{\partial \nu(\mu)}{\partial \mu}\right]^2 \\ & + -\frac{1}{2}\frac{\partial f(f(f(\nu)))}{\partial f(f(\nu))} \cdot \frac{\partial^2 f(f(\nu))}{\partial f(\nu)^2} \cdot \left[\frac{\partial f(\nu)}{\partial \nu} \cdot \frac{\partial \nu(\mu)}{\partial \mu}\right]^2 \\ & + -\frac{1}{2}\frac{\partial f(f(f(\nu)))}{\partial f(f(\nu))} \cdot \frac{\partial f(f(\nu))}{\partial f(\nu)} \cdot \frac{\partial^2 f(\nu)}{\partial \nu^2} \cdot \left[\frac{\partial \nu(\mu)}{\partial \mu}\right]^2 \\ & + -\frac{1}{2}\frac{\partial f(f(f(\nu)))}{\partial f(f(\nu))} \cdot \frac{\partial f(f(\nu))}{\partial f(\nu)} \cdot \frac{\partial f(\nu)}{\partial \nu} \cdot \frac{\partial^2 \nu(\mu)}{\partial \mu^2} \tag{A.9}\end{aligned}$$

Appendix B

DFT utils

B.1 Functional quantities

The full list of quantities needed from the density functionals is

$$f = f(\rho_\alpha, \rho_\beta, \gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta}) \tag{B.1}$$

$$\frac{\partial f}{\partial \rho_\alpha} \tag{B.2}$$

$$\frac{\partial f}{\partial \rho_\beta} \tag{B.3}$$

$$\frac{\partial f}{\partial \gamma_{\alpha\alpha}} \tag{B.4}$$

$$\frac{\partial f}{\partial \gamma_{\alpha\beta}} \tag{B.5}$$

$$\frac{\partial f}{\partial \gamma_{\beta\beta}} \tag{B.6}$$

$$\frac{\partial^2 f}{\partial \rho_\alpha \partial \rho_\alpha} \tag{B.7}$$

$$\frac{\partial^2 f}{\partial \rho_\beta \partial \rho_\alpha} \tag{B.8}$$

$$\frac{\partial^2 f}{\partial \gamma_{\alpha\alpha} \partial \rho_\alpha} \tag{B.9}$$

$$\frac{\partial^2 f}{\partial \gamma_{\alpha\beta} \partial \rho_\alpha} \tag{B.10}$$

$$\frac{\partial^2 f}{\partial \gamma_{\beta\beta} \partial \rho_\alpha} \tag{B.11}$$

$$\frac{\partial^2 f}{\partial \rho_\beta \partial \rho_\beta} \tag{B.12}$$

$$\frac{\partial^2 f}{\partial \gamma_{\alpha\alpha} \partial \rho_\beta} \tag{B.13}$$

$$\frac{\partial^2 f}{\partial \gamma_{\alpha\beta} \partial \rho_\beta} \tag{B.14}$$

$$\frac{\partial^2 f}{\partial \gamma_{\beta\beta} \partial \rho_\beta} \tag{B.15}$$

$$\frac{\partial^2 f}{\partial \gamma_{\alpha\alpha} \partial \gamma_{\alpha\alpha}} \tag{B.16}$$

$$\frac{\partial^2 f}{\partial \gamma_{\alpha\beta} \partial \gamma_{\alpha\alpha}} \tag{B.17}$$

$$\frac{\partial^2 f}{\partial \gamma_{\beta\beta} \partial \gamma_{\alpha\alpha}} \tag{B.18}$$

$$\frac{\partial^2 f}{\partial \gamma_{\alpha\beta} \partial \gamma_{\alpha\beta}} \tag{B.19}$$

$$\frac{\partial^2 f}{\partial \gamma_{\beta\beta} \partial \gamma_{\alpha\beta}} \tag{B.20}$$

$$\frac{\partial^2 f}{\partial \gamma_{\beta\beta} \partial \gamma_{\beta\beta}} \tag{B.21}$$

$$\tag{B.22}$$

B.2 Derivatives of basis functions

For the second derivative code we need the second derivatives of the gradient of the density. This implies that we need third derivatives of the basis functions. A basis function is constructed from three factors of the form

$$\chi_x = x^p \exp(-\alpha x^2) \tag{B.23}$$

To construct 3rd derivatives we all derivatives upto 3rd order, i.e.

$$\frac{\partial \chi_x}{\partial x} = (px^{p-1} - 2\alpha x^{p+1}) \exp(-\alpha x^2) \tag{B.24}$$

$$\frac{\partial^2 \chi_x}{\partial x^2} = (p[p-1]x^{p-2} - 2\alpha[2p+1]x^p + 4\alpha^2 x^{p+2}) \exp(-\alpha x^2) \tag{B.25}$$

$$\frac{\partial^3 \chi_x}{\partial x^3} = (p[p-1][p-2]x^{p-3} - 6\alpha p^2 x^{p-1}) \exp(-\alpha x^2)$$
$$+ (12\alpha^2[p+1]x^{p+1} - 8\alpha^3 x^{p+3}) \exp(-\alpha x^2) \tag{B.26}$$

The derivative of a basis function with respect to a nuclear coordinate differs depending on whether we need to include the derivative quadrature or not.

The basis functions are defined as

$$\chi_\mu(R^A, r) = (r_x - R_x^A)^p (r_y - R_y^A)^q (r_z - R_z^A)^r$$

$$\cdot \quad \exp(-\alpha[(r_x - R_x^A)^2 + (r_y - R_y^A)^2 + (r_z - R_z^A)^2]) \text{ (B.27)}$$

differentiating this basis function with respect to R_x^C gives

$$\frac{\partial \chi_\mu(R^A, r)}{\partial R_x^C} = 0 \tag{B.28}$$

if $A \neq C$ and

$$
\begin{aligned}
\frac{\partial \chi_\mu(R^A, r)}{\partial R_x^C} &= [-p(r_x - R_x^A)^{p-1}(r_y - R_y^A)^q(r_z - R_z^A)^r \\
&+ 2\alpha(r_x - R_x^A)^{p+1}(r_y - R_y^A)^q(r_z - R_z^A)^r] \\
&\cdot \exp(-\alpha[(r_x - R_x^A)^2 + (r_y - R_y^A)^2 + (r_z - R_z^A)^2]) \text{(B.29)}
\end{aligned}
$$

otherwise.

However, if the grid point is associated with an atom then we have

$$
\begin{aligned}
\chi_\mu(R^A, r^B) &= (R_x^B + r_x - R_x^A)^p(R_y^B + r_y - R_y^A)^q(R_z^B + r_z - R_z^A)^r \\
&\cdot \exp(-\alpha[(R_x^B + r_x - R_x^A)^2 + (R_y^B + r_y - R_y^A)^2 \\
&+ (R_z^B + r_z - R_z^A)^2]) \tag{B.30}
\end{aligned}
$$

differentiating this function with respect to R_x^C gives

$$\frac{\partial \chi_\mu(R^A, r^B)}{\partial R_x^C} = 0 \tag{B.31}$$

if $C \neq A$ and $C \neq B$ or if $C = A = B$. However if $C = A \neq B$ then

$$
\begin{aligned}
\frac{\partial \chi_\mu(R^A, r^B)}{\partial R_x^C} &= [-p(R_x^B + r_x - R_x^A)^{p-1}(R_y^B + r_y - R_y^A)^q(R_z^B + r_z - R_z^A)^r \\
&+ 2\alpha(R_x^B + r_x - R_x^A)^{p+1}(R_y^B + r_y - R_y^A)^q(R_z^B + r_z - R_z^A)^r] \\
&\cdot \exp(-\alpha[(R_x^B + r_x - R_x^A)^2 + (R_y^B + r_y - R_y^A)^2 \\
&+ (R_z^B + r_z - R_z^A)^2]) \tag{B.32}
\end{aligned}
$$

on the other hand if $C = B \neq A$ then

$$
\begin{aligned}
\frac{\partial \chi_\mu(R^A, r^B)}{\partial R_x^C} &= [p(R_x^B + r_x - R_x^A)^{p-1}(R_y^B + r_y - R_y^A)^q(R_z^B + r_z - R_z^A)^r \\
&- 2\alpha(R_x^B + r_x - R_x^A)^{p+1}(R_y^B + r_y - R_y^A)^q(R_z^B + r_z - R_z^A)^r] \\
&\cdot \exp(-\alpha[(R_x^B + r_x - R_x^A)^2 + (R_y^B + r_y - R_y^A)^2 \\
&+ (R_z^B + r_z - R_z^A)^2]) \tag{B.33}
\end{aligned}
$$

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