

# 1 Common Notation

We will use C1 symmetry and assume an RHF reference throughout.

Index classes to be used include,

$\mu, \nu, \lambda, \sigma$ : Primary basis functions, i.e., atomic orbitals (AOs)  $\{\phi_\mu(\vec{r})\}$ . The size of this index is given by  $n$ .

$i, j$ : Canonical occupied orbitals, i.e., occupied molecular orbitals (MOs)  $\{\psi_i(\vec{r})\}$ . The size of this index is given by  $o$ .

$a, b$ : Canonical virtual orbitals, i.e., unoccupied molecular orbitals (MOs)  $\{\psi_a(\vec{r})\}$ . The size of this index is given by  $v$ .

$A, B, C, D$ : Auxiliary basis functions used in density fitting, i.e.,  $\{\chi_A(\vec{r})\}$ . The size of this index is given by  $Q$ .

$\zeta, \eta$ : CPHF perturbations, particularly the dipole operators  $\hat{x}$ ,  $\hat{y}$ , and  $\hat{z}$  in the computation of the dipole polarizability.

$I$ : CPHF iteration number.

In general,  $o$  is one third to one tenth of  $n$ ,  $v$  is roughly  $n$ , and  $Q$  is three to five times  $n$ .

We also use the “generalized Einstein summation convention” which essentially means that we refuse to write the summation symbols in the equations. Any index which disappears is assumed to be summed over, e.g., in matrix multiplication,

$$C_{ij} = A_{ik}B_{kj} \Rightarrow C_{ij} = \sum_{k=1}^{N_k} A_{ik}B_{kj} \quad (1)$$

## 2 LibFock: CPHF for Dipole Polarizabilities

In this section, we will outline the mathematical steps behind solving the Coupled-Perturbed Hartree-Fock (CPHF) equations for the dipole polarizability tensor.

### 2.1 Quick Physics:

If you apply a static force  $F$  to a mass on a spring, the mass will displace by distance  $x$  according to  $kx = -F$  (usually pronounced  $F = -kx$ ). Here  $k$  is the spring force constant  $k = \partial^2 E / \partial x^2$ . Similarly, if you apply a set of static forces  $\vec{F}$  to a set of masses connected by springs, the masses will displace by  $\vec{x}$  according  $\hat{k}_{ij}\vec{x}_j = -\vec{F}_i$ , where the Hessian or stiffness matrix  $\hat{k}$  is defined as  $\hat{k}_{ij} = \partial^2 E / \partial x_i \partial x_j$ .

Now, let us apply this idea to a Hartree-Fock wavefunction. In this case, if we apply some external field, the electrons could respond by exciting from the occupied orbitals to the virtual orbitals<sup>1</sup>. Therefore, the displacements of the system are best parametrized by the singles excitation amplitudes  $\vec{x} \rightarrow x_{ia}$ . The corresponding forces applied to the system are  $-\vec{F} \rightarrow f_{ia}$ . The corresponding stiffness matrix is  $H_{ia,jb}$ , the electronic Hessian, leading to the Coupled-Perturbed Hartree-Fock equations,

$$H_{ia,jb}x_{jb} = f_{ia}$$

The leading term in the Hessian is the diagonal contribution  $(\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab}$ , which accounts for the energy penalty of exciting from orbital  $i$  to orbital  $a$ . If only the leading term is applied in the Hessian, the electrons all excite independently of one another, i.e., they are uncoupled. In reality, the electrons are all coupled to one another through the mean-field potential: two-body effects must be added to account for this coupling. Applying this treatment leads to the electronic Hessian and CPHF equations.

## 2.2 CPHF Implementation:

The CPHF equations for an RHF reference are,<sup>2</sup>

$$\underbrace{\{(\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + [4(ia|jb) - (ib|ja) - (ij|ab)]\}}_{H_{ia,jb}} x_{jb}^\zeta = f_{ia}^\zeta \quad (2)$$

The elements  $f_{ia}^\zeta$  are the perturbation forces, which for dipole polarization are the dipole integrals,<sup>3</sup>

$$f_{ia}^\zeta = \{-2(i|\hat{x}|a), -2(i|\hat{y}|a), -2(i|\hat{z}|a)\} \quad (3)$$

Once the CPHF equations are solved, the elements of the  $3 \times 3$  static dipole polarizability tensor are obtained as,

$$\gamma^{\zeta\eta} = -x_{ia}^\zeta f_{ia}^\eta \quad (4)$$

If we explicitly consider the matrix  $H_{ia,jb}$ , we set that we are just solving the set of linear equations,

$$H_{ia,jb}x_{jb}^\zeta = f_{ia}^\zeta \quad (5)$$

We could exactly solve these equations, but this would cost  $\mathcal{O}(o^3v^3)$  FLOPs and would require storage of the  $\mathcal{O}(o^2v^2)$  electronic Hessian. Instead, we will use the structure of the equations to perform an iterative solution. It is easily seen that the above may be re-written as,

$$x_{ia}^\zeta = \frac{f_{ia}^\zeta - [4(ia|jb) - (ib|ja) - (ij|ab)]x_{jb}^\zeta}{\epsilon_a - \epsilon_i} \quad (6)$$

<sup>1</sup>This can also be viewed as a change of orbitals from the optimal Hartree-Fock solution to new orbitals which are optimal under the perturbation, i.e., an orbital rotation.

<sup>2</sup>These are written in terms of electron pairs.

<sup>3</sup>2 for a pair of electrons, minus for  $-F \rightarrow f_{ia}$ .

What we will do is to make some guess for  $x_{ia}^\zeta$ , substitute into the right-hand size of the above, and get a new guess for  $x_{ia}^\zeta$  on the left-hand side. We will then iterate until  $x_{ia}^\zeta$  stops changing, to within some convergence criterion,<sup>4</sup>

$$x_{ia}^{\zeta,(I+1)} \leftarrow \frac{f_{ia}^\zeta - [4(ia|jb) - (ib|ja) - (ij|ab)] x_{jb}^{\zeta,(I)}}{\epsilon_a - \epsilon_i} \quad (7)$$

Note that if we substitute  $x_{ia}^{\zeta,(0)} = 0$ , we obtain the uncoupled result,

$$x_{ia}^{\zeta,(1)} = \frac{f_{ia}^\zeta}{\epsilon_a - \epsilon_i} \quad (8)$$

Therefore, we see that the rest of the CPHF iterations are adding two-body coupling effects to the uncoupled solution.

The next critical realization is that we never need any explicit four-index tensors, but instead only need products of the four-index tensors with successive guesses for  $x_{ia}^\zeta$ . That is, if we define the function  $H^{(2)}[q_{jb}^\zeta]$  as,

$$H^{(2)}[q_{jb}^\zeta] \equiv [4(ia|jb) - (ib|ja) - (ij|ab)] q_{jb}^\zeta, \quad (9)$$

we see that the iterative procedure may be written as,

$$x_{ia}^{\zeta,(I+1)} \leftarrow \frac{f_{ia}^\zeta - H^{(2)}[x_{jb}^{\zeta,(I)}]}{\epsilon_a - \epsilon_i}, \quad (10)$$

If we have some black-box way to get  $H^{(2)}[q_{jb}^\zeta]$ , then we have an iterative CPHF procedure involving only order-2 tensors!

The last key trick is to realize that the two-body contributions  $H^{(2)}[q_{jb}^\zeta]$  can be written in terms of generalized Fock matrix builds. Considering the definition of the MO-basis ERIs, e.g.,

$$(ia|jb) = C_{\mu i} C_{\nu a} (\mu\nu|\lambda\sigma) C_{\lambda j} C_{\sigma b}, \quad (11)$$

we can selectively back-transform to the AO-basis. Defining, the generalized density matrix (not symmetric),

$$D_{\lambda\sigma}^\zeta[q_{jb}^\zeta] \equiv \underbrace{C_{\lambda j}}_{L_{\lambda j}} \underbrace{q_{jb}^\zeta C_{\sigma b}}_{R_{\sigma j}} \quad (12)$$

We can form the two-body contributions as,

$$H^{(2)}[q_{jb}^\zeta] \equiv [4(ia|jb) - (ib|ja) - (ij|ab)] q_{jb}^\zeta \quad (13)$$

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<sup>4</sup>This is called direct iteration, and only works because the diagonal contribution  $(\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab}$  dominates  $H_{ia,jb}$ .

$$= C_{\mu i} \left\{ 4 \underbrace{(\mu\nu|\lambda\sigma)D_{\lambda\sigma}^{\zeta}}_{J_{\mu\nu}[D_{\lambda\sigma}^{\zeta}]} - \underbrace{(\mu\sigma|\lambda\nu)D_{\lambda\sigma}^{\zeta}}_{K_{\nu\mu}[D_{\lambda\sigma}^{\zeta}]} - \underbrace{(\mu\lambda|\sigma\nu)D_{\lambda\sigma}^{\zeta}}_{K_{\mu\nu}[D_{\lambda\sigma}^{\zeta}]} \right\} C_{\nu a}$$

The quantities  $J_{\mu\nu}[D_{\lambda\sigma}^{\zeta}]$  and  $K_{\mu\nu}[D_{\lambda\sigma}^{\zeta}]$  are just generalized Coulomb and exchange matrices! The generalized Coulomb matrix is always symmetric, the generalized exchange matrix is generally not. Therefore, if we were to write a piece of code that generated generalized Coulomb and exchange matrices efficiently, we could reuse it in Hartree-Fock, CPHF, and actually many other places. In PSI4, this object is called JK, and is part of the larger LibFock project. An additional point is that we always find a factorization of the generalized density matrix of the form  $D_{\mu\nu} = L_{\mu i}R_{\nu i}$  found in Equation 12, analogous to the factorization of the usual SCF OPDM as  $D_{\mu\nu} = C_{\mu i}C_{\nu i}$ . Generalized Fock builds based on density fitting technology can exploit the smaller size of  $o$  compared to  $n$  provided by this factorization. Today, we will implement a production-level code for the CPHF dipole polarizability tensor using the machinery of LibFock.

### 3 LibTHCE: Density-Fitted MP2

In this section, we will outline the mathematical steps behind computing the density fitted (DF) second-order Møller-Plesset Perturbation Theory (MP2) correlation energy.

The MP2 correlation energy in canonical orbitals, for an RHF reference, is,

$$E_{\text{MP2}} = 2 \underbrace{\frac{(ia|jb)(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{E_{\text{MP2J}}} - \underbrace{1 \frac{(ia|jb)(ib|ja)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{E_{\text{MP2K}}} \quad (14)$$

The first contribution is ‘‘Coulomb-like’’ (MP2J), the second is ‘‘exchange-like’’ (MP2K).

The rate-limiting portion of MP2 is the formation of the chemists’s integrals  $(ia|jb)$ , which usually involves a four-index integral transformation,<sup>5</sup>

$$(ia|jb) = C_{\mu i}C_{\nu a}(\mu\nu|\lambda\sigma)C_{\lambda j}C_{\sigma b} \quad (15)$$

Conventionally, this is done one index at a time, with considerable disk storage of the and sorting of the intermediates,

$$(i\nu|\lambda\sigma) \leftarrow C_{\mu i}(\mu\nu|\lambda\sigma) \quad \mathcal{O}(on^4) \quad (16)$$

$$(i\nu|j\sigma) \leftarrow C_{\lambda j}(i\nu|\lambda\sigma) \quad \mathcal{O}(o^2n^3) \quad (17)$$

$$(ia|j\sigma) \leftarrow C_{\nu a}(i\nu|j\sigma) \quad \mathcal{O}(o^2vn^2) \quad (18)$$

<sup>5</sup>Note that it is possible to use generalized Fock builds to compute the MP2 energy, as above, but  $\mathcal{O}(N^2)$  builds are required, yielding a procedure which is  $\mathcal{O}(N^6)$ . While this is not immediately useful, it turns out that the generalized density matrices involved can be made to be very sparse, so that each Fock matrix construction may be nearly constant scaling with some effort in screening. This approach is used in many local MP2 implementations, and in the MBIE MP2J work of Ochsenfeld.

$$(ia|jb) \leftarrow C_{\sigma b}(ia|j\sigma) \quad \mathcal{O}(\sigma^2 v^2 n) \quad (19)$$

In density fitting, we know that the integrals can be approximately, but very accurately represented as a low-rank product of two three-index quantities,<sup>6</sup>

$$(\mu\nu|\lambda\sigma) \approx (\mu\nu|A)(A|B)^{-1}(B|\lambda\sigma) = b_{\mu\nu}^C b_{\lambda\sigma}^C \quad (20)$$

Here, we define the symmetrically-fitted three-index integrals as,

$$b_{\mu\nu}^C \equiv (C|B)^{-1/2}(B|\mu\nu) \quad (21)$$

In DF-MP2, we avoid the nasty  $\mathcal{O}(N^5)$  integral transformation by performing the integral transformation on the three-index quantities, and *then* zipping the three-index quantities together to build the needed four-index MO integrals. This is extremely useful in MP2, because we only need integrals of  $(ov|ov)$ -type (i.e., not all MO-basis integrals are needed). Under this paradigm, there are two phases to a DF-MP2 computation. The first phase is a three-index integral transformation and fitting step,

$$b_{ia}^C = C_{\mu i} C_{\nu a} b_{\mu\nu}^C = C_{\mu i} C_{\nu a} (C|B)^{-1/2}(B|\mu\nu) \quad (22)$$

In practice this is done as,

$$(B|i\nu) \leftarrow C_{\mu i}(B|\mu\nu) \quad \mathcal{O}(on^2Q) \quad (23)$$

$$(B|ia) \leftarrow C_{\nu a}(B|i\nu) \quad \mathcal{O}(onvQ) \quad (24)$$

$$b_{ia}^C \leftarrow (C|B)^{-1/2}(B|ia) \quad \mathcal{O}(ovQ^2) \quad (25)$$

Note that the fitting is delayed until after the AO-to-MO transformation: the  $(Q|ov)$  integrals are much smaller than the  $(Q|nn)$  integrals, so the fitting is much cheaper if it is left until last.

The second phase is the generation of the needed four-index MO-basis integrals from the three-index tensors,

$$(ia|jb) \approx b_{ia}^C b_{jb}^C \quad \mathcal{O}(\sigma^2 v^2 Q) \quad (26)$$

and the subsequent summation of the MP2 energy, according to Equation 14.

In DF-MP2, we traded a  $\mathcal{O}(on^4)$  integral transformation involving  $\mathcal{O}(on^3)$  disk storage for a single  $\mathcal{O}(\sigma^2 v^2 Q)$  integral assembly step and only  $\mathcal{O}(ovQ)$  disk storage. Because of savings in FLOP count, disk storage, and integral generation, DF-MP2 is usually an order of magnitude faster than conventional MP2, and quite easy to thread.

Today, we will write a production-level code for the generation of the DF-MP2 energy. We will obtain the  $ov$ -type three-index tensor of Equation 22 from the `libTHCE` library, and then assemble the integrals of Equation 26 via matrix multiplication, for each unique  $ij$  pair. A note is appropriate regarding storage: as a general rule of thumb, order-1 tensors (vectors) always fit in core, order-2 tensors (matrices) almost always fit in core, order-3

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<sup>6</sup>We are using the Coulomb metric in the fitting here, as is almost always done.

tensors (density-fitting tensors) fit in core only up to 1000 basis functions, and order-4 tensors (integrals) fit in core only up to 200-300 basis functions, and run out of disk at about 1000 basis functions. For DF-MP2, we should be able to run up to several thousand basis functions, so we will disk block all order-3 tensors, and never explicitly store any order-4 tensors.