Periodic exchange interactions evaluated in real space

- Exchange energy with periodicity

$$E_x^{PBC-\Gamma} = -\frac{1}{2}\sum_{i,j}\iint_{\infty} \psi_i(r_1)\psi_j(r_1)\frac{1}{r_{12}}\psi_i(r_2)\psi_j(r_2)\,dr_1\,dr_2$$

$$\psi_i(r) = \sum_{\mu\vec{a}} C^{\mu i}\phi_\mu^{\vec{a}}$$

- Precontract $\sum_i C^{\mu i}C^{\lambda i} \rightarrow P^{\mu\lambda}$
- Consider energy per unit supercell:

$$-\frac{1}{2}\sum_{\mu}\sum_{\nu\vec{a}}\sum_{\lambda\vec{b}}\sum_{\sigma\vec{c}} P^{\mu\lambda}P^{\nu\sigma}\iint \phi_\mu^{\vec{0}}(1)\phi_\nu^{\vec{a}}(1)\frac{1}{r_{12}}\phi_\lambda^{\vec{b}}(2)\phi_\sigma^{\vec{b}+\vec{c}}(2)d_1d_2$$

$$-\frac{1}{2}\sum_{\mu}\sum_{\nu\vec{a}}\sum_{\lambda\vec{b}}\sum_{\sigma\vec{c}} P^{\mu\lambda}P^{\nu\sigma}\iint \phi_{\mu}^{\vec{0}}(1)\phi_{\nu}^{\vec{a}}(1)\frac{1}{r_{12}}\phi_{\lambda}^{\vec{b}}(2)\phi_{\sigma}^{\vec{b}+\vec{c}}(2)d_1 d_2$$

Convergence with a and c rapid $\phi_{\mu}(r_1)\phi_{\nu}^{\vec{a}}(r_1)\to 0$
so can rapidly truncate lattice series with overlap criterion.

Sum over b is conditionally convergent: Consider

$$e_{\nu\lambda} = -\frac{1}{2}\sum_{\vec{b}}(P^{\nu\lambda})^2(\phi_{\nu}^{0}\phi_{\nu}^{0}\,|\,\phi_{\lambda}^{\vec{b}}\phi_{\lambda}^{\vec{b}}) \sim -\sum_{\vec{b}}^{|b|^{d-1}}\frac{P^2}{4|\vec{b}|}$$

- Traditional ways around this are to simply select one b which minimizes distance between electrons (MIC) – unstable
- In k-space can use analytic auxiliary function
- Instead, truncate kernal (good for relatively isotropic cells

$$g_{TC}(r_{12}) = \begin{cases} \dfrac{1}{r_{12}} & \text{If } r < Rc \\ 0 & \text{else} \end{cases}$$

- Sum over b now rigorously truncates
- <ii|ii> terms only cancel in the TDL

Interfaces

```
call ExactExchange(P,X,Ex)
   real, intent(in) :: P(nBF,nBF)    !density matrix
   real, intent(out) :: X(nAO,nAO*nBF) !Exchange matrix
   real, intent(out) :: Ex     !Exchange energy
```

Need to think about how exactly it is to be symmetry packed?

External calls

1) Will need to modify Geralds code for a new TC integral kernal: $(\phi_\mu^{\vec{0}}\phi_\nu^{\vec{a}} \mid g_{TC} \mid \phi_\lambda^{\vec{b}}\phi_\sigma^{\vec{b}+\vec{c}})$

$$G_0(\rho,T,R'_c) = \frac{\pi^{3/2}}{2\rho}\frac{2erf(\sqrt{T}) + erf(R'_c - \sqrt{T}) - erf(R'_c + \sqrt{T})}{\sqrt{T}}$$

Call for

2) Will require/be instructive to have overlap integrals for screening & convergence of a &c?

N^4 scaling – most expensive part of HF