Ewald summation @ Waffle 0.1

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The context

In the Fock operator

$$\hat{f}\psi_i(\vec{r}) = \left(-\frac{1}{2}\vec{\nabla}^2 - \sum_A \frac{Z_A}{\mid \vec{r}_A - \vec{r} \mid} + \int \frac{\rho(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} d\vec{r}' \right) \psi_i(\vec{r}) - \sum_j \int d\vec{r}' \left(\frac{\psi_j^*(\vec{r}')\psi_i(\vec{r}')}{\mid \vec{r}' - \vec{r} \mid} \right) \delta_{s_i^z, s_j^z} \psi_j(\vec{r})$$

we can shift charge between the nuclear and direct electronic terms

$$\tilde{\rho}_N(\vec{r}) = -\sum_A Z_A \delta(\vec{r} - \vec{r}_A) + \frac{N}{\Omega} \quad (1)$$

$$\tilde{\rho}_e(\vec{r}) = \rho(\vec{r}) - \frac{N}{\Omega} \quad (2)$$

without changing the global charge distribution or the HF equations. This allows both terms to be treated separately, the direct electronic part by FFT and the nuclear part by Ewald summation.

Exact expressions

One can show that

$$\int \frac{\tilde{\rho}_N(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} d\vec{r}' = -\sum_A Z_A \frac{\mathrm{erfc}\left(\frac{\sqrt{\eta}}{2} \mid \vec{r} - \vec{r}_A \mid\right)}{\mid \vec{r} - \vec{r}_A \mid} + \frac{4\pi N}{\Omega \eta} - \frac{4\pi}{\Omega} \sum_\alpha Z_\alpha \sum_{\mathbf{G} \neq 0} \frac{e^{i\mathbf{G}.(\vec{r} - \vec{r}_\alpha)} e^{-G^2/\eta}}{G^2} \quad (3)$$

A: all charges
α: charges in one supercell
N: total number of electrons per supercell
G: reciprocal lattice vectors of the supercell
Ω: supercell volume
η: self-introduced parameter

- erfc decays exponentially fast: summation in real space OK.
- $e^{-G^2/\eta}$: summation in reciprocal space OK.
- All terms can be sandwiched between Gaussian primitives analytically.
  - first term: Gerald's code
  - second term: just the overlap
  - third term: our code: class Ewald

Reciprocal sum

- void Ewald_pt1::eN(double * result, double ζ_A, int $lmax_A$, double Ax, double Ay, double Az, double ζ_B, int $lmax_B$, double Bx, double By, double Bz);
- Provide array result of size $\frac{(lmax_A+1)(lmax_A+2)}{2} \times \frac{(lmax_B+1)(lmax_B+2)}{2}$.
- count is defined e.g. for lmax = 3:

count	(n_x, n_y, n_z)
0	(3,0,0)
1	(2,1,0)
2	(2,0,1)
3	(1,2,0)
4	(1,1,1)
5	(1,0,2)
6	(0,3,0)
7	(0,2,1)
8	(0,1,2)
9	(0,0,3)

- Fills in result $\left[count_A + \frac{(lmax_A+1)(lmax_A+2)}{2} count_B \right]$ with

$$\int (x-Ax)^{n_x^A} (y-Ay)^{n_y^A} (z-Az)^{n_z^A} (x-Bx)^{n_x^B} (y-By)^{n_y^B} (z-Bz)^{n_z^B} \tag{4}$$

$$e^{-\zeta_A(\vec{r}-\vec{A})^2} e^{-\zeta_B(\vec{r}-\vec{B})^2} \left(-\frac{4\pi}{\Omega} \sum_\alpha Z_\alpha \sum_{\mathbf{G}\neq 0} \frac{e^{i\mathbf{G}.(\vec{r}-\vec{r}_\alpha)} e^{-G^2/\eta}}{G^2} \right) d\vec{r} \tag{5}$$

- Real-valued sine & cosine recursion relations are implemented per coordinate axis.

Nuclear-nuclear term

- The following approximation is made in the program:

$$\tilde{E}_{direct} + \tilde{E}_{eN} = \frac{1}{2}\int\int \frac{\rho(\vec{r})\tilde{\rho}_e(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} d\vec{r}d\vec{r}' + \int\int \frac{\rho(\vec{r})\tilde{\rho}_N(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} d\vec{r}d\vec{r}' \tag{6}$$

- The remainder of the exact electrostatic energy is

$$\tilde{E}_{remainder} = \frac{1}{2}\int\int \frac{\rho_N(\vec{r}+\vec{\epsilon})\rho_N(\vec{r}')}{\mid \vec{r} - \vec{r}' + \vec{\epsilon} \mid} d\vec{r}d\vec{r}' - \frac{1}{2}\sum_A \frac{Z_A^2}{\mid \vec{\epsilon} \mid} - \frac{1}{2}\frac{N}{\Omega}\int\int \frac{\rho(\vec{r})}{\mid \vec{r} - \vec{r}' \mid} d\vec{r}d\vec{r}' \tag{7}$$

  with $\rho_N(\vec{r}) = -\sum_A Z_A \delta(\vec{r} - \vec{r}_A)$ and $\vec{\epsilon}$ going to zero.

- Make the approximation $\rho(\vec{r}) = \rho_N(\vec{r})$ in the last term.
- The nuclear-nuclear term (per supercell) is then given by

$$W = \sum_{\alpha\beta} \frac{Z_\alpha Z_\beta}{2} \left(\frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq 0} \frac{e^{i\mathbf{G}.(\vec{r}_{\beta\alpha})} e^{-G^2/\eta}}{G^2} - \sqrt{\frac{\eta}{\pi}}\delta_{\alpha\beta} + \sum_{\mathbf{T}}{}' \frac{\mathrm{erfc}\left(\frac{\sqrt{\eta}}{2} \mid \vec{r}_{\beta\alpha} + \mathbf{T} \mid\right)}{\mid \vec{r}_{\beta\alpha} + \mathbf{T} \mid} \right) - \frac{4\pi N^2}{2\Omega\eta} \tag{8}$$

  with $\vec{r}_{\beta\alpha} = \vec{r}_\beta - \vec{r}_\alpha$. The ' denotes that the self-interaction term is explicitly kept out for the case $\mathbf{T} = 0$.

- double Ewald_pt1::NN()