Periodic Fast Multipole Method

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Input

- Supercell geometry
- Nuclei (xyz, charge)
- AO basis set
- 1PDM

Output

Coulomb matrix elements due to macroscopic potential,

$$J_{\alpha\beta} = \sum_k \int\int \alpha(\mathbf{r}) \frac{\rho_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \beta(\mathbf{r}) \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{1}$$

where k runs over supercells and excludes nearest-neighbours. $\rho_k(\mathbf{r})$ is the density in supercell k.

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Hydrogen molecular crystal

Consider:

- One H2 in each supercell, 2 s-functions.
- i.e. 2 nuclear charges, and 3 spherical electronic charge distributions.
- Zero total charge and dipole in each supercell.
  Therefore expect convergence.
- Interact all 5 charges in distant supercells with 3 electronic charges in reference cell.

Results: Direct summation

- 27*27*27 supercells.
- Excluded space is 3*3*3 supercells.
- Consider interaction energy of reference cell with far field.

No multipoles

No. interactions = 9 * (27**3 - 3**3) = 9 * 19656

e-n + e-e = -0.1583861788 E_h

One multipole expansion per supercell

No. interactions = 27**3 - 3**3 = 19656

tLMAX	e-n + e-e
20	-0.1583845309
25	-0.1583860391
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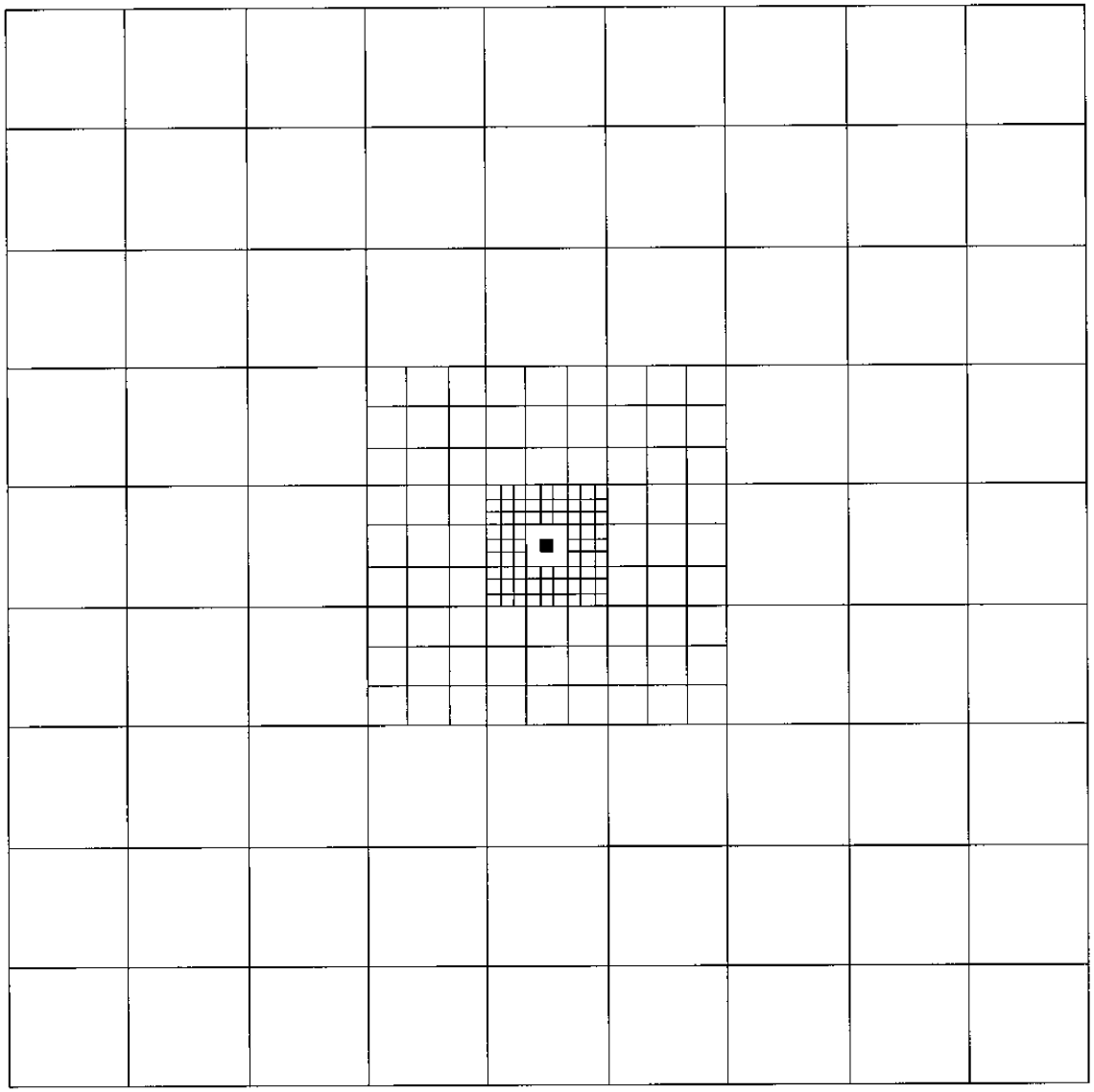
PFMM aggregation of distant supercells



Results: PFMM summation

tLMAX = 40; 702 cell-cell interactions per PFMM level

levels	CellD	PFMM	Exact
2	27	-0.1583861788	-0.1583861788
3	81	-0.1597806926	-0.1597806926
4	243	-0.1599356149	-0.1599356149
5	729	-0.1599528312	-0.1599528312
6	2187	-0.1599547707	
7	6561	-0.1599552259	
8	19683	-0.1599574334	
9	59049	-0.1599770916	
10	177147	-0.1601539918	
11	531441	-0.1617460911	
12	1594323	-0.1760749843	
13	4782969	-0.3050350231	
14	14348907	-1.4656753724	
15	43046721	-11.911438516	

Appears to be some numerical instability for large volumes??

What's next?

- Include short-range contribution from excluded volume (nearest-neighbour supercells).
- Use Gerald's code <–> Very similar issue to George's exchange integrals.
- Nothing is interfaced to the main code yet!
- Modify to account for supercells with non-zero total dipole.