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https://www.ur.de/physics/wilhelm/teaching/sose24-computational-nanoscience

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Computational Nanoscience: Solution to Exercise Sheet No. 4

Exercise 4.1: Computational scaling of Hartree-Fock

(a) Both increase linearly with N_atom, so N^1_atom. The number of occupied molecular orbitals increases linearly with the number of electrons, that also increases linearly with the number of atoms (if we only add the same atom type).

(b) The scaling of an operation with N^α_atom is determined by the number of different indices that are appearing (the size of the index itself needs to scale linearly with N_atom). The calculation of the Hartree and exchange potential matrix elements,

$$V^\text{H}_{\mu\nu} = 2\sum_{m=1}^{N/2}\sum_{\lambda\sigma}(\mu\nu|\lambda\sigma)\, C_{m\lambda}C_{m\sigma}\,, \tag{1}$$

$$V^\text{x}_{\mu\nu} = -\sum_{m=1}^{N/2}\sum_{\lambda\sigma}(\mu\lambda|\nu\sigma)\, C_{m\lambda}C_{m\sigma}\,, \tag{2}$$

requires therefore $O(N^5_\text{atom})$ multiplications (5 indices: μ,ν,λ,σ,m), which is the highest scaling in the Hartree-Fock algorithm.

(c) Using the density matrix

$$D_{\lambda\sigma} = \sum_{m=1}^{N/2} C_{m\lambda}\, C_{m\sigma}\,, \tag{3}$$

we can rewrite the upper computations as

$$V^\text{H}_{\mu\nu} = 2\sum_{\lambda\sigma}(\mu\nu|\lambda\sigma)\, D_{\lambda\sigma}\,, \tag{4}$$

$$V^\text{x}_{\mu\nu} = -\sum_{\lambda\sigma}(\mu\lambda|\nu\sigma)\, D_{\lambda\sigma}\,. \tag{5}$$

Now, we have 4 indices left and the scaling of these operations is therefore $O(N^4_\text{atom})$.

(d) A Gaussian basis function

$$\phi_\nu(\mathbf{r}) = Y_{lm}(\varphi,\theta)\,\exp(-\beta|\mathbf{r}-\mathbf{R}_A|^2) \tag{6}$$

is centred at an atom A. The two-centre integrals

$$S_{\mu\nu} = \int d^3\mathbf{r}\;\phi_\mu(\mathbf{r})\,\phi_\nu(\mathbf{r}) \tag{7}$$

are vanishingly small with a decay $\exp(-\gamma|\mathbf{R}_A-\mathbf{R}_B|^2)$ if any two of the atoms A and B to which the basic functions belong are far enough apart (compared to the length scale of the Gaussians), where

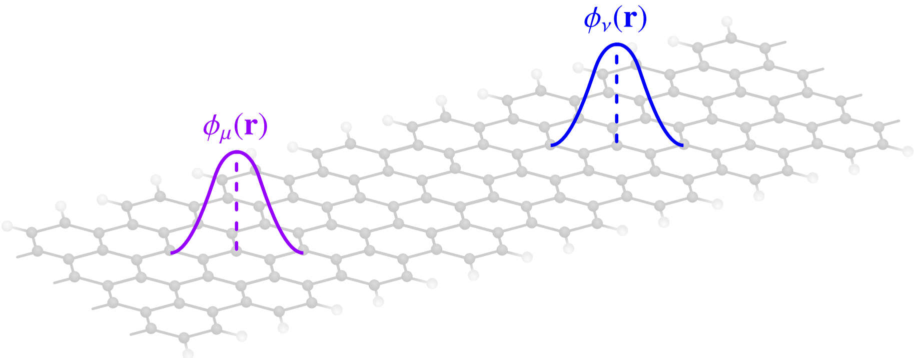

Figure 1: Two Gaussian basis functions on a large molecule.

γ is determined by the exponents β of the Gaussians $\phi_\mu(\mathbf{r})$ and $\phi_\nu(\mathbf{r})$.

For a small numerical value of the four-centre integral

$$(\mu\nu|\lambda\sigma) = \iint d^3\mathbf{r}\, d^3\mathbf{r}'\ \phi_\mu(\mathbf{r})\,\phi_\nu(\mathbf{r})\ \frac{1}{|\mathbf{r}-\mathbf{r}'|}\ \phi_\lambda(\mathbf{r}')\,\phi_\sigma(\mathbf{r}') \tag{8}$$

the product $\phi_\mu(\mathbf{r})\,\phi_\nu(\mathbf{r})$ or the product $\phi_\lambda(\mathbf{r}')\,\phi_\sigma(\mathbf{r}')$ needs to become vanishingly small. Similarly as in $S_{\mu\nu}$, the value of a product $\phi_\mu(\mathbf{r})\,\phi_\nu(\mathbf{r})$ is exponentially small for any position $\mathbf{r}$ if the atomic centres $\mathbf{R}_A$ of $\phi_\mu(\mathbf{r})$ and $\mathbf{R}_B$ of $\phi_\nu(\mathbf{r})$ are far apart. That means, the four-centre integral $(\mu\nu|\lambda\sigma)$ will have a small numerical value, if the atomic centres of ϕ_μ and ϕ_ν are far apart or if the atomic centres of ϕ_λ and ϕ_σ are far apart.

(e) With the consideration from (d), the number of 4c integrals that need to be kept is $O(N_\text{atom}^2)$:

- We need to use all ϕ_μ, but only the ϕ_ν that are close to ϕ_μ (so we have the first N_atom factor).
- We need to use all ϕ_λ, but only the ϕ_σ that are close to ϕ_λ (so we have the second N_atom factor).

What happens, if ϕ_μ and ϕ_λ are far apart (while ϕ_ν is close to ϕ_μ and ϕ_σ is close to ϕ_λ)? Answer: The integral is slightly smaller compared to the case where ϕ_μ and ϕ_λ are close, but the decay is only $1/|\mathbf{R}_A - \mathbf{R}_B|$ ($\mathbf{R}_A$ is centre of ϕ_μ and $\mathbf{R}_B$ is centre of ϕ_λ). Consider a spread of a Gaussian function of around 1 Å defining the length scale of the Coulomb interaction. With a molecule of ca. 20 Å size as proposed in the exercise, the largest distance between basis functions is 20 Å and by the decay of the Coulomb operator, we have just a decrease of 1/20 for the 4c integrals. This decay is not sufficient to remove the integrals from the calculation.

Summarizing, $O(N_\text{atom}^2)$ 4c integrals need to be kept in the calculation.

(f) In such a scenario, the computation of $V^\text{x}_{\mu\nu}$ and $V^\text{H}_{\mu\nu}$ scales as $O(N_\text{atom}^2)$. Therefore, one of the $O(N_\text{atom}^3)$ scaling steps will dominate the Hartree-Fock calculation time in the limit of large systems, for example the diagonalisation of the Fock matrix that scales with $O(N_\text{atom}^3)$.

(g) I obtained

Number of H_2 molecules, N_{H_2}	CPU time (s)
1	1.083
2	1.903
4	23.541
6	92.218
8	269.496

If you have obtained slightly different numbers, this could have various reasons.

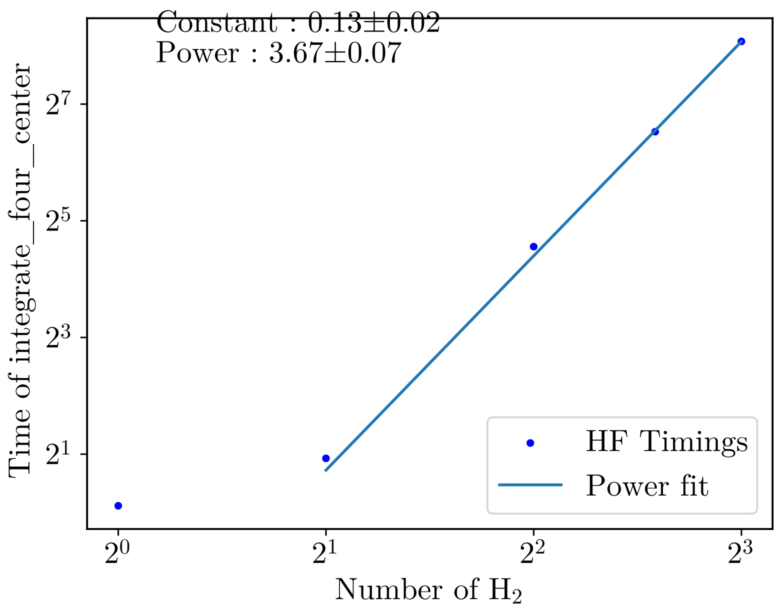

Figure 2: Time of qs_energies routine on 12 threads in seconds. Due to expected power law, we show the log-log scale.

(h) I got an exponent of 3.52 from 4 $H_2 \rightarrow$ 8 H_2 and an exponent of 3.63 from 2 $H_2 \rightarrow$ 4 H_2.

(i) Since all atoms are close (by construction in our input file), all four-centre integrals need to be calculated and kept and the highest exponent in the canonical Hartree-Fock algorithm will be $O(N_{\text{atom}}^4)$. But there are also other steps that scale as $O(N_{\text{atom}}^{\alpha})$ with $\alpha < 4$, which may have a larger prefactor and contribute significantly to the CPU time for small systems.

Furthermore, the parallel efficiency of the code generally increases with increasing system size, which is the reason why we are in fact observing a slightly slower scaling than $O(N_{\text{atom}}^4)$.