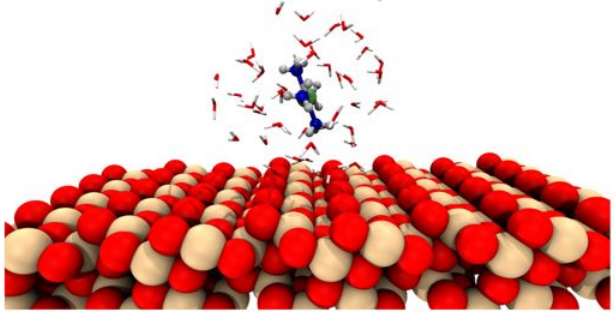
Introduction to electronic structure calculations

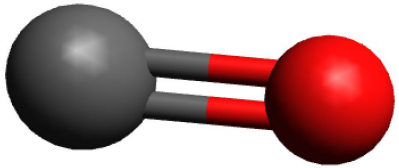
QM/MM and ab initio Molecular Dynamics
Summer School
June 23 – June 27, 2025



Solving for physical quantities using DFT outputs

Mario F. Borunda

Vibrations of an isolated molecule



Bond length: $b = x_C - x_O$

Taylor expansion of energy:

$$E = E_o + (b - b_0)\left[\frac{dE}{db}\right]_{b=b_0} + \frac{1}{2}(b - b_0)^2 + \left[\frac{d^2E}{db^2}\right]_{b=b_0} + \ldots$$

Harmonic approximation:

$$E = E_o + \frac{\alpha}{2}(b - b_0)^2; \alpha = \left[\frac{d^2E}{db^2}\right]_{b=b_0}$$

A little algebra...

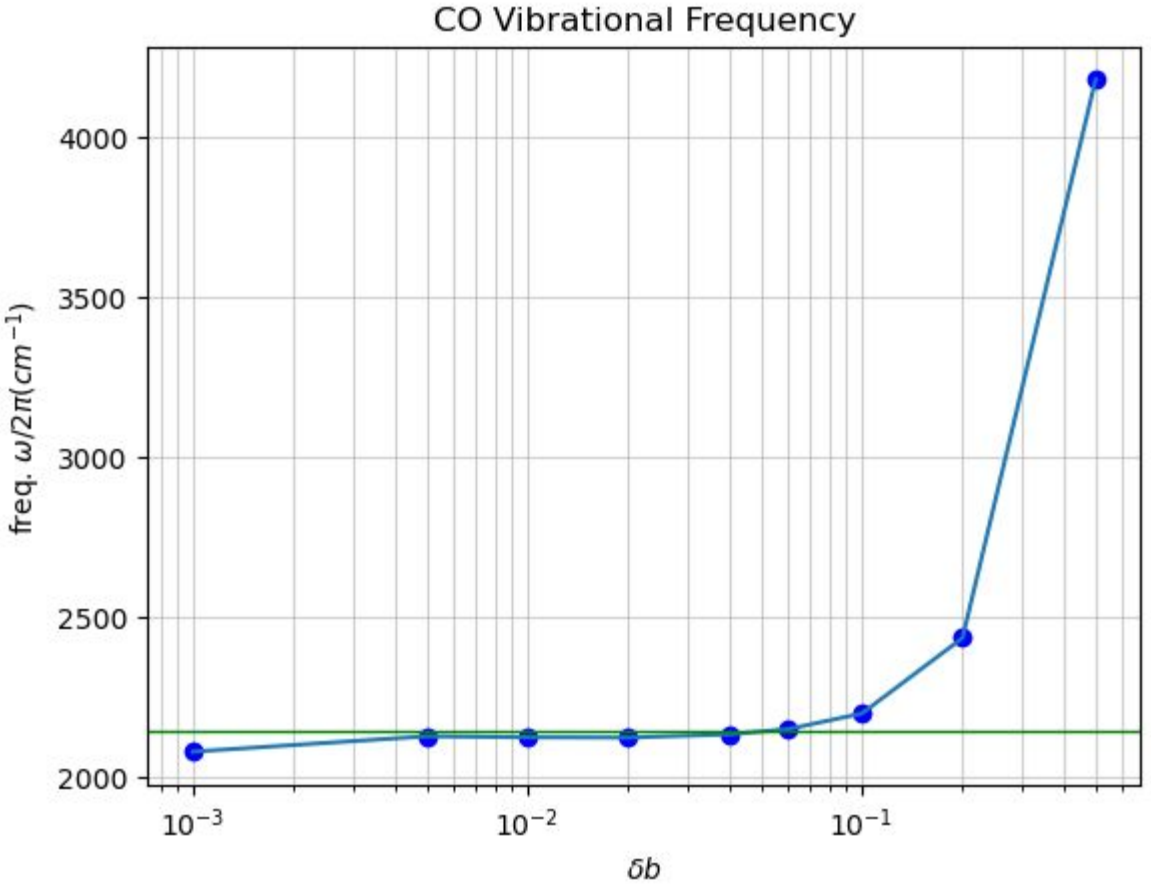
$$\frac{d^2b(t)}{dt^2} = -\alpha\left(\frac{m_C + m_O}{m_C m_O}\right)(b(t) - b_0)$$

Solving the PDE...

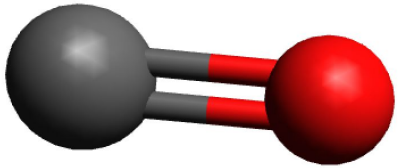
$$b(t) = b_0 + a\cos\omega t$$

$$\omega^2 = \alpha\frac{m_C + m_O}{m_C m_O}$$

Using finite differences: $\alpha = \left[\frac{d^2E}{db^2}\right]_{b=b_0} \approx \frac{E(b_0+\delta b) - 2E(b_0) + E(b_0-\delta b)}{(\delta b)^2}$



Another approach: Time dependent



From a Molecular-Dynamics run, obtain the Velocity Autocorrelation

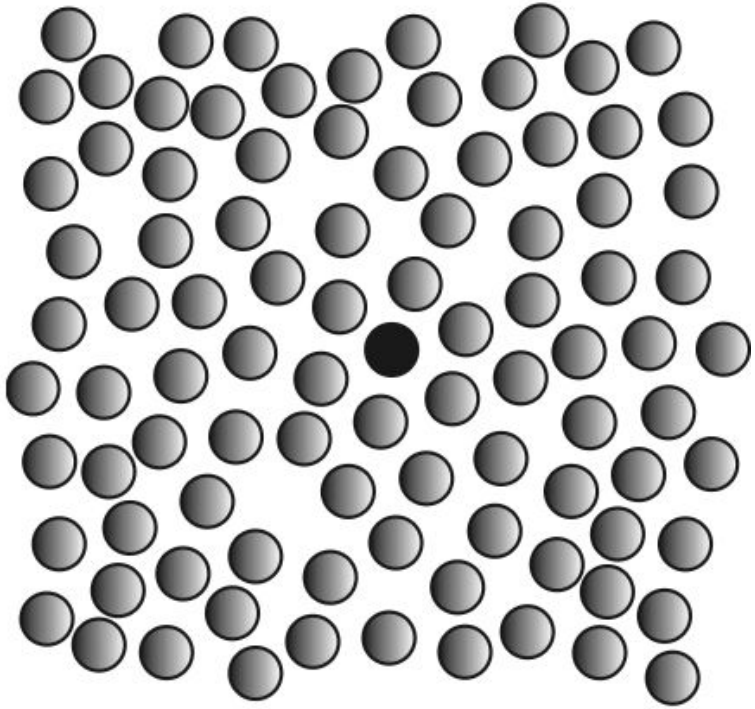
$$C_v(t) = \sum_{i=1}^{N_{atoms}} \vec{v_i}(t) \cdot \vec{v_i}(t_0)$$

The mdanalysis.py utility can calculate the velocity autocorrelation

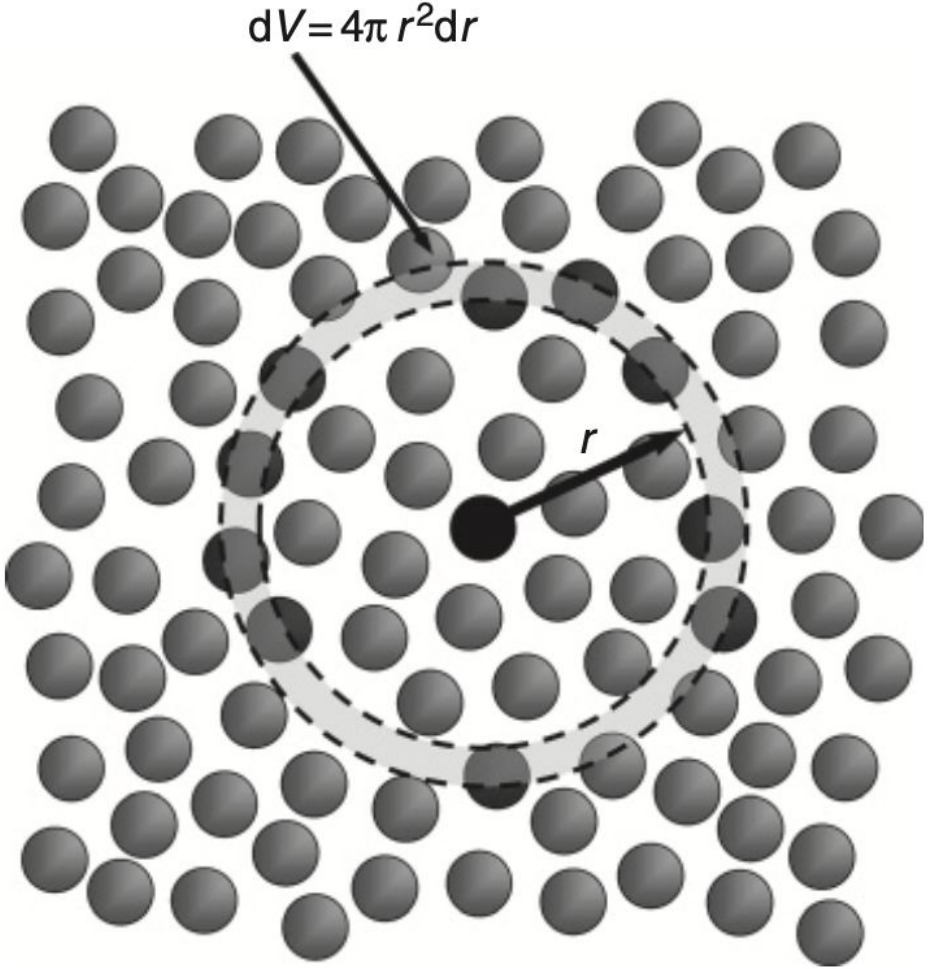
Afterwards, we can calculate the spectrum by taking the Fourier transform of the data.

Python scripts…

Amorphous Structures



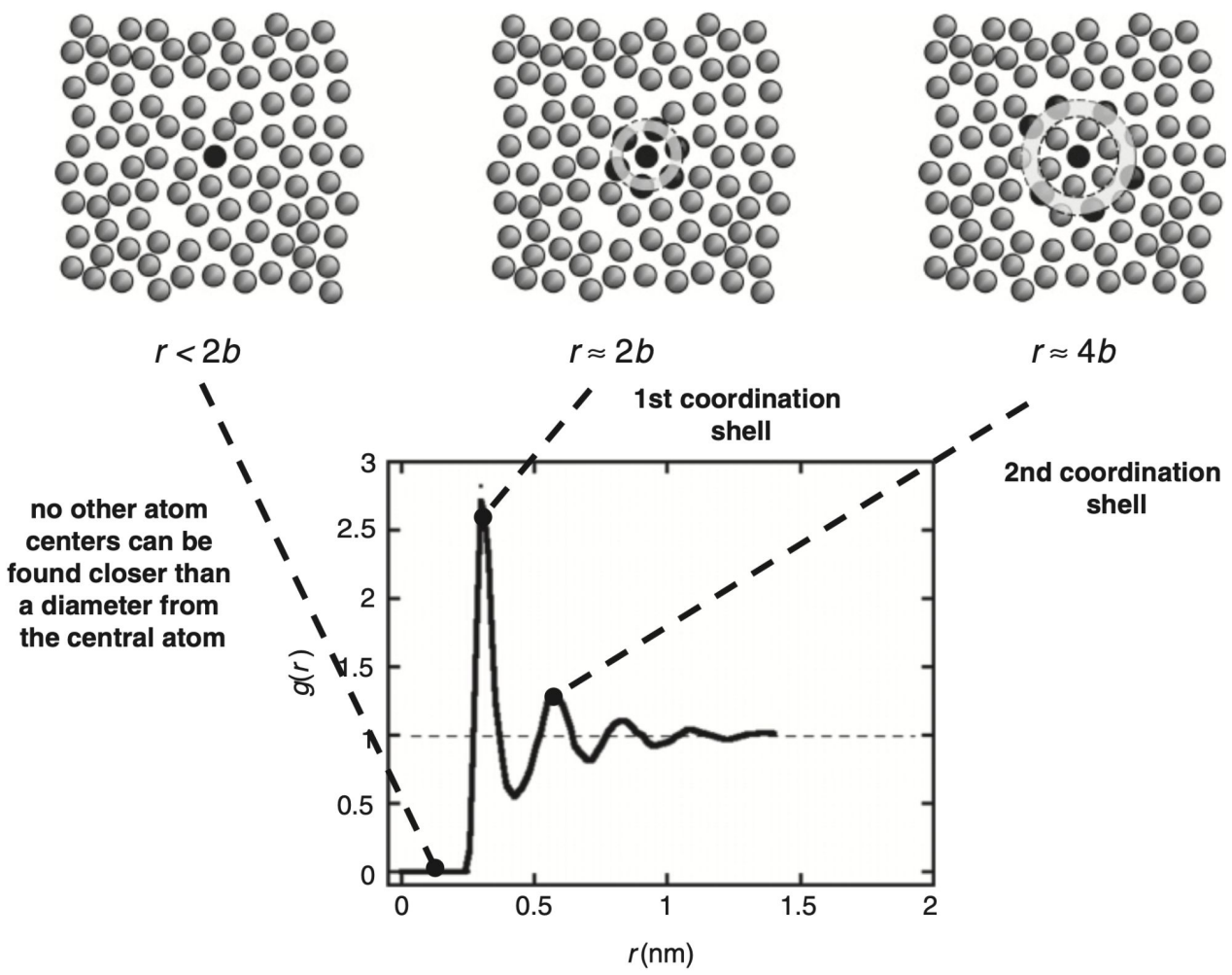
Observations?



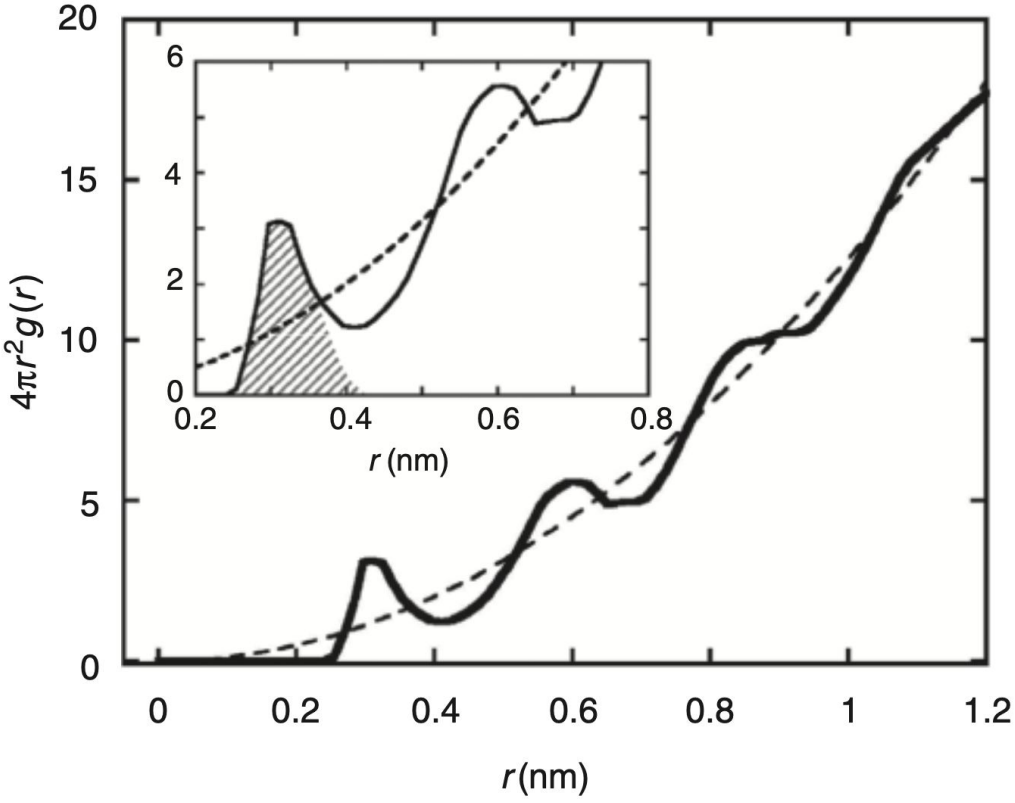
$$g(\vec{r}_1, \vec{r}_2) \rightarrow g(r).$$

$$g(r) \propto \left\langle \frac{\#\text{ particle centers in dV}}{4\pi r^2 \mathrm{d}r} \right\rangle,$$

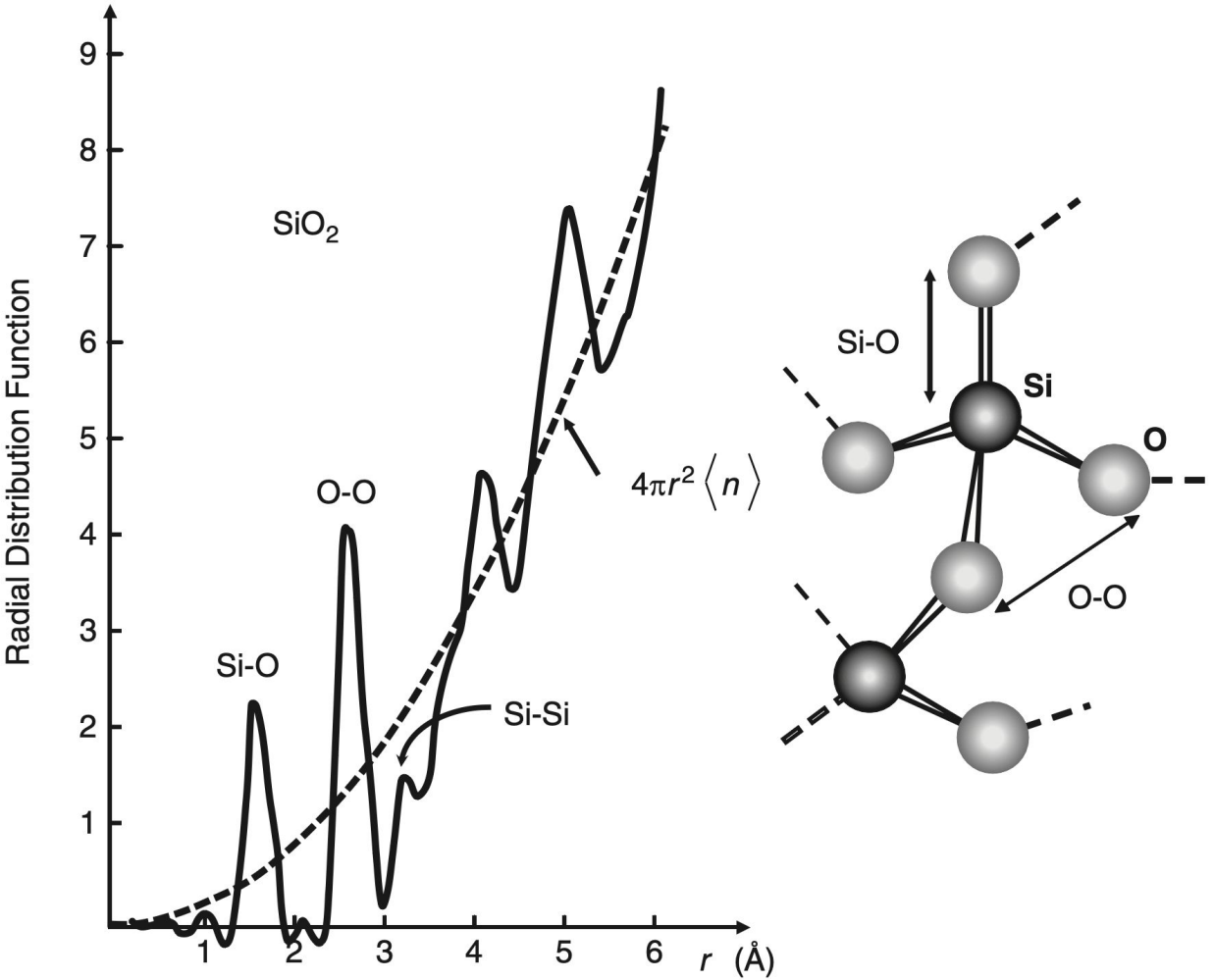
$$g(r) = \frac{\langle n(r) \rangle_{\text{excl}}}{\langle n \rangle} = \frac{1}{\langle n \rangle} \left\langle \frac{\#\text{ particle centers in dV}}{4\pi r^2 \mathrm{d}r} \right\rangle.$$


r < 2b
r ≈ 2b
r ≈ 4b
1st coordination shell
2nd coordination shell
no other atom centers can be found closer than a diameter from the central atom
g(r)
r(nm)
0
0.5
1
1.5
2
2.5
3

Radial distribution function & Coordination numbers



$$\langle \#\ \text{particle centers in dV} \rangle = \langle n \rangle g(r) 4\pi r^2 \mathrm{d}r.$$


Radial Distribution Function
9
8
7
6
5
4
3
2
1
SiO_2
O-O
Si-O
Si-Si
$4\pi r^2 \langle n \rangle$
1
2
3
4
5
6
r (Å)
Si-O
Si
O
O-O

Improving the Density of Jammed Disordered Packings Using Ellipsoids

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