Webinar 06 – Geometry Optimization (Part 2)

Administrative updates

The Bilbao Crystallographic Server is currently unavailable due to a ransomware incident. A temporary backup link has been provided for this course; while not all tools are guaranteed to work, the essentials for this module are available. If you used publicly accessible alternatives for the green crystallographic information blocks that appeared in several reports, please share the link so it can be added to the course site.

For larger calculations and project work, enable parallel execution (see last week's notes and the Zulip thread). When scaling from a small to a larger—but similar—cell, adjust the k-point mesh proportionally: doubling the size along z allows halving the k-mesh in z (e.g., $10\times10\times10 \rightarrow 10\times10\times5$). For a $2\times2\times2$ supercell, a $\sim 5\times5\times5$ grid typically suffices instead of $10\times10\times10$, saving substantial compute time.

If disk space is an issue in Quantum ESPRESSO, consider `disk_io` and `wfcdir` settings to reduce file output. This may increase RAM usage and can prevent restarting from intermediate states, but it saves space.

Correcting prior work based on feedback is encouraged. Redoing calculations to obtain sound results is an intended part of the learning process.

1) Background on forces

In both classical and quantum mechanics, forces are the negative derivatives of the total energy with respect to atomic coordinates. In quantum mechanics, the Hellmann–Feynman theorem simplifies evaluation of these derivatives, which would otherwise involve complicated matrix elements.

2) Position optimization in Fe–Al (orthorhombic, Pmmn, No. 59)

Using space-group information, Fe occupies Wyckoff 2a and Al occupies 2b. In both cases, z is a free internal coordinate, while x and y are fixed by symmetry. Consequently, forces act only along z for these sites.

Computed forces on symmetry-related pairs are equal in magnitude and opposite in sign, pointing along $\pm z$. Upon relaxation, z increases where the force points upward and decreases where it points downward, as expected. Some misinterpretations in reports stemmed from sign reading rather than incorrect calculations.

Why symmetry still shows up in P1 inputs: High-symmetry positions are typically extrema of the energy landscape. Small displacements tend to return atoms toward the symmetric minimum. Spontaneous symmetry breaking only occurs when the local landscape admits nearby competing minima (e.g., a shallow double-well). Also note that the free z parameters on different Wyckoff sites are independent; do not tie them to the same value.

3) Interpreting Quantum ESPRESSO coordinates

Quantum ESPRESSO may print positions in fractional coordinates or in *alat* units. Determine *alat*, construct lattice vectors, and divide *alat*-scaled coordinates by the corresponding vector lengths to recover fractional values (e.g., 1/4, 3/4, and the site-specific z parameters).

4) Magnitudes and convergence

Typical displacements upon relaxation are small but meaningful (e.g., $\Delta z \approx 0.014$ in fractional units, ~ 0.06 Å). Forces below ~ 1 mRy/bohr are effectively converged to zero; forces above ~ 10 mRy/bohr are large. Energy lowerings of a few mRy per four-atom cell are common. Reported volume changes during position-only relaxation should be minimal; large apparent drops typically indicate unit-conversion errors.

5) Degrees of freedom in the Fe–Al example

There are two internal degrees of freedom (the two independent z parameters on 2a and 2b) and three lattice parameters (a, b, c) for the orthorhombic cell: five degrees of freedom in total. Conceptually, optimization damps motion in each degree of freedom until the system reaches the minimum.

6) Full optimization (vc-relax) and the stress tensor

Full optimization adjusts atomic positions and cell shape/volume simultaneously using the stress tensor. This is straightforward in plane-wave codes such as Quantum ESPRESSO. The procedure finds the best structure near your initial guess; it will not jump to distant prototypes (e.g., a cesium-chloride structure) unless the starting geometry is already close.

7) Input "recipes"

- Volume & cell-shape scans: `calculation='scf'` (static energies only; no geometry changes).
- Position optimization: `calculation='relax'` with an `&IONS` block (choose the algorithm); cell fixed.
- Full optimization: `calculation='vc-relax'` with `&IONS` and `&CELL` (cell algorithm, target pressure; default is ~ 0 GPa).

8) Why full optimization matters

Accurate bulk moduli require optimizing the structure at each sampled volume. If you keep shape and internal positions fixed while varying the volume, the $E(V)$ curve is biased and the curvature (hence bulk modulus) is overestimated. The same principle applies to phase-stability comparisons: skipping optimization can lead to qualitatively wrong conclusions.

9) Phase diagrams and formation energies

For Fe–Al, the CsCl prototype consistently has a more negative formation energy (e.g., ~ -0.30 eV/atom) than the orthorhombic prototype (e.g., ~ -0.15 eV/atom), with modest numerical scatter depending on optimization depth.

The convex-hull construction identifies thermodynamically stable phases as those on the lower envelope of formation energy versus composition. Points above the hull decompose into the neighboring hull phases at fixed composition. Databases may be incomplete; consult multiple sources where possible.

Practical workflow for complex compositions: After a converged, fully optimized calculation of your candidate, use a database (e.g., OQMD with its GCLP routine) to identify the most competitive phases at the same composition. Compute their total energies with identical settings, form the weighted sum, and compare with your candidate to assess stability.

10) Looking ahead

Next week focuses on electronic structure: band structures and densities of states. Please submit a short summary of your key takeaways from this week and propose at least one exam question.