
Certificate in Quantum Espresso And VASP Theory

Quantum Espresso Basics

ABINIT – first-principles software – A computational package that, like Quantum Espresso (QE), solves the Kohn-Sham equations using plane-wave basis sets. Example: ABINIT can be used to benchmark QE total-energy calculations for silicon. Practical application: Cross-checking phonon frequencies. Challenge: Ensuring consistent pseudopotentials across the two codes.

ACE – adaptively compressed exchange – An algorithm that accelerates hybrid functional calculations in QE by compressing the exact-exchange operator. Example: ACE reduces the cost of HSE06 calculations on a 64-atom supercell. Practical application: Enabling hybrid-functional studies of defects. Challenge: Memory overhead for large systems.

Band Structure – energy-momentum relation – The dispersion of electronic eigenvalues $\epsilon_n(\mathbf{k})$ across the Brillouin zone, visualised as lines connecting high-symmetry \mathbf{k} -points. Example: The band structure of graphene shows Dirac cones at K. Practical application: Predicting metallic versus insulating behaviour. Challenge: Converging \mathbf{k} -point meshes and dealing with band-crossing ambiguities.

Brillouin Zone – reciprocal-space primitive cell – The Wigner-Seitz cell of the reciprocal lattice; the domain for \mathbf{k} -point sampling. Example: For a cubic lattice, the Brillouin zone is a cube centred at Γ . Practical application: Determining the minimal set of \mathbf{k} -points for accurate total energies. Challenge: Handling reduced symmetry in low-symmetry crystals.

Cell Optimization – variable-cell relaxation – A QE calculation that simultaneously relaxes atomic positions and lattice vectors to minimise the stress tensor. Example: Using "vc-relax" to find the equilibrium lattice constant of Al. Practical application: Predicting pressure-induced phase transitions. Challenge: Choosing appropriate convergence thresholds for forces and stresses.

Charge Density – $\rho(\mathbf{r})$ – The electron density obtained from the occupied Kohn-Sham states; the central variable of density-functional theory (DFT). Example: Visualising $\rho(\mathbf{r})$ in VESTA reveals bonding regions in NaCl. Practical application: Constructing electrostatic potentials for surface calculations. Challenge: Achieving sufficient plane-wave cutoff to resolve rapid density variations near nuclei.

COHP – crystal orbital Hamilton population – A post-processing analysis that partitions the density of states into bonding, antibonding, and non-bonding contributions. Example: COHP analysis of Fe-O bonds in hematite clarifies magnetic interactions. Practical application: Interpreting chemical bonding in complex oxides. Challenge: Requires accurate projections and careful selection of energy windows.

Conjugate Gradient – iterative minimisation – An algorithm used in QE for electronic self-consistency and ionic relaxation, efficient for large systems. Example: The "cg" algorithm converges the wavefunctions of a 200-atom polymer chain. Practical application: Speeding up geometry optimisations. Challenge: May stall for metallic systems with poor preconditioning.

Core-Level Spectroscopy – X-ray absorption, EELS – Simulations based on the linear response of core electrons, often performed with QE's "xspectra" module. Example: Calculating the K-edge of carbon in diamond. Practical application: Interpreting experimental XANES spectra. Challenge: Need for accurate core-hole pseudopotentials and large supercells.

Cutoff Energy – E_{cut} – The maximum kinetic energy of plane waves included in the basis set; determines the size of the reciprocal-space grid. Example: An E_{cut} of 60 Ry yields converged total energies for Si. Practical application: Balancing computational cost and accuracy. Challenge: Different pseudopotentials demand different cutoffs; convergence tests are mandatory.

Density of States (DOS) – $g(\epsilon)$ – The distribution of electronic states per energy interval; obtained by smearing the discrete eigenvalues. Example: A metallic DOS shows finite value at the Fermi level. Practical application: Estimating carrier concentrations. Challenge: Choosing appropriate smearing methods (Gaussian, Methfessel-Paxton) to avoid artificial features.

DFT+U – Hubbard correction – An extension of DFT that adds an on-site Coulomb term to better describe localized d or f electrons. Example: Applying $U=4$ eV to Ni-d states improves band gaps of NiO. Practical application: Modelling strongly correlated oxides. Challenge: Selecting the correct U value; dependence on the chosen pseudopotential.

DFPT – density-functional perturbation theory – A linear-response method implemented in QE to compute phonons, dielectric constants, and electron-phonon coupling without finite-difference supercells. Example: Computing the phonon dispersion of MgO using "ph.X". Practical application: Predicting lattice-thermal conductivity. Challenge: Handling metallic systems where smearing affects the response.

Dipole Correction – slab electrostatics – A technique that adds a compensating field to remove spurious interactions between periodic images of a polar slab. Example: Adding a dipole correction for a water-on-metal surface simulation. Practical application: Accurate work-function calculations. Challenge: Determining the correct vacuum thickness and dipole plane.

Elastic Constants – C_{ij} – Second-order derivatives of the total energy with respect to strain; obtained via DFPT or finite-difference strain–stress calculations. Example: Computing C_{11} for cubic Fe. Practical application: Assessing mechanical stability of novel alloys. Challenge: Convergence with respect to k-points and strain magnitude.

Electron-Phonon Coupling (EPC) – λ , $\alpha^2F(\omega)$ – Quantifies the interaction strength between electrons and phonons, crucial for superconductivity studies. Example: Using QE's "lambda.X" to evaluate λ for MgB₂. Practical application: Estimating critical temperatures via the McMillan formula. Challenge: Dense q-point sampling and accurate Wannier interpolation are required.

Fermi Surface – k-space constant-energy sheet – The set of k-points where $\epsilon_n(\mathbf{k})=E_F$; visualised to understand metallic transport. Example: Plotting the Fermi surface of Cu reveals nested sheets. Practical application: Analysing nesting-driven instabilities. Challenge: Requires extremely fine k-meshes and careful interpolation.

Fermi-Level Smearing – occupancy broadening – A technique to aid SCF convergence for metals by spreading electron occupations over a small energy window. Example: Methfessel-Paxton smearing of 0.02 Ry for Al. Practical application: Stabilising metallic calculations. Challenge: Smearing influences total energies; post-processing may need extrapolation to zero smearing.

Force Constant Matrix – Φ – The second derivative of the total energy with respect to atomic displacements; obtained from DFPT phonon calculations. Example: Constructing Φ for a 2-atom primitive cell of NaCl. Practical application: Building dynamical matrices for phonon dispersion. Challenge: Ensuring translational invariance and acoustic sum rule compliance.

G-vector – reciprocal-space plane-wave index – The vector defining each plane-wave basis function; its magnitude is limited by the cutoff energy. Example: G-vectors with $|G| \leq \sqrt{2 E_{\text{cut}}}$ are included. Practical application: controlling basis-set size. Challenge: large G-vectors increase memory and CPU time.

Hybrid Functionals – PBE0, HSE06 – Exchange-correlation approximations that mix a fraction of exact Hartree-Fock exchange with DFT exchange. Example: HSE06 improves the band gap of GaAs from 0.5 eV (PBE) to 1.4 eV. Practical application: Accurate band-gap predictions for semiconductors. Challenge: Computational cost scales steeply with system size; ACE or screened-exchange techniques are needed.

In-Plane Lattice Constant – a, b – Lattice parameters parallel to a surface slab; often fixed to experimental values when modelling epitaxial strain. Example: Setting $a = b = 3.905 \text{ \AA}$ for SrTiO₃(001) slab. Practical application: Simulating strain-engineered thin films. Challenge: Mismatch between substrate and film may require large supercells.

Input File – pw.X, ph.X, etc. – The plain-text file that controls a QE calculation; contains &CONTROL, &SYSTEM, &ELECTRONS, and atomic specifications. Example: The &SYSTEM block defines `ecutwfc`, occupations, and smearing. Practical application: Reproducible simulations. Challenge: Syntax errors and missing required flags often cause runtime failures.

K-point Sampling – Monkhorst-Pack grid – The discretisation of the Brillouin zone into a set of k-points; defined by an integer mesh (e.g., $6 \times 6 \times 6$). Example: A $4 \times 4 \times 4$ grid suffices for a 20-atom organic crystal. Practical application: Balancing accuracy and cost. Challenge: Metallic systems need denser meshes; convergence tests are essential.

Local Density Approximation (LDA) – uniform-electron gas – An exchange-correlation functional that assumes the electron density is locally homogeneous. Example: LDA predicts a lattice constant of 4.04 Å for Al, slightly underestimated. Practical application: Quick structural optimisations. Challenge: Systematic under-binding; fails for van-der-Waals systems.

Magnetic Moment – μ_B – The spin polarisation per atom, obtained from spin-polarised QE calculations. Example: Fe in bcc Fe carries $\sim 2.2 \text{ MB}$. Practical application: Designing magnetic materials. Challenge: Convergence of spin density can be sensitive to initial magnetisation and smearing.

Non-collinear Magnetism – spinor wavefunctions – An extension of spin-polarised DFT that allows the magnetisation direction to vary spatially. Example: Modelling a spin-spiral in Cr using

"noncolin=True.&Quot;. Practical application: Studying complex magnetic textures. Challenge: Increased computational cost and need for fully relativistic pseudopotentials.

Occupations – smearing, fixed – Specification of how electron occupations are assigned to Kohn-Sham states; determines metallic vs insulating treatment. Example: &Quot;occupations='smearing', smearing='gaussian', degauss=0.01&Quot;. Practical application: Stabilising SCF loops. Challenge: Inappropriate smearing can distort total energies and forces.

PAW – projector-augmented wave – A pseudopotential method that reconstructs all-electron wavefunctions from smooth pseudo-wavefunctions. Example: QE's PAW dataset for Cu includes 3d and 4s valence. Practical application: High-accuracy total-energy differences with modest cutoffs. Challenge: Generating reliable PAW datasets; compatibility with hybrid functionals.

Phonon Dispersion – $\omega(\mathbf{q})$ – The variation of phonon frequencies with wavevector; obtained from DFPT or finite-difference supercells. Example: The acoustic branches of Si show linear behaviour near Γ . Practical application: Assessing dynamical stability of new materials. Challenge: Ensuring the acoustic sum rule and dealing with imaginary modes.

Plane-Wave Basis – Fourier expansion – The set of plane-wave functions used to expand Kohn-Sham orbitals; controlled by the cutoff energy. Example: A 70 Ry cutoff yields $\sim 10\,000$ plane-waves for a 2-atom cell. Practical application: Systematic convergence with a single parameter. Challenge: Large memory footprints for high-cutoff calculations.

Projected Density of States (PDOS) – atom-resolved DOS – Decomposition of the total DOS onto atomic orbitals or angular momentum channels. Example: PDOS shows that O-2p states dominate the valence band of TiO_2 . Practical application: Interpreting spectroscopic data. Challenge: Selection of projection radii and orthogonalisation schemes.

Quantum ESPRESSO (QE) – open-source DFT suite – A collection of codes (pw.X, ph.X, cp.X, etc.) For electronic-structure calculations based on plane-waves and pseudopotentials. Example: Using pw.X for ground-state calculations, ph.X for phonons. Practical application: Research, teaching, and high-throughput workflows. Challenge: Steep learning curve for newcomers; careful input preparation required.

Quasi-Particle GW – self-energy correction – A many-body perturbation method that improves band energies by adding a self-energy $\Sigma = i\text{GW}$. Example: GW0 raises the Si band gap from 0.6 eV (PBE) to 1.1 eV. Practical application: Accurate electronic excitations. Challenge: Computationally demanding; requires well-converged DFT starting points.

Relaxation – ionic optimisation – The process of moving atoms to minimise forces, often combined with cell optimisation. Example: A "relax" run reduces forces below 0.001 Ry/Bohr for a water molecule. Practical application: Obtaining equilibrium structures. Challenge: Trapped in local minima; need for varied initial geometries.

SCF Cycle – self-consistent field – Iterative procedure that updates the electron density until convergence criteria are met. Example: Convergence reached when $\Delta E_{\text{smearing}}$ Methods – Gaussian, Methfessel-Paxton,

Marzari-Vanderbilt – Techniques to broaden electron occupations; each has different impact on total energy and forces. Example: Methfessel-Paxton order 1 is common for metals; Gaussian is preferred for insulators. Practical application: Improving SCF stability. Challenge: Selecting degauss small enough to avoid artificial thermal effects.

Spin-Orbit Coupling (SOC) – relativistic interaction – Inclusion of the coupling between electron spin and its orbital motion; essential for heavy elements. Example: SOC splits the valence band of PbTe, affecting thermoelectric properties. Practical application: Topological insulator studies. Challenge: Requires fully relativistic pseudopotentials and doubles the size of spinor wavefunctions.

Supercell – periodic expansion – A larger cell constructed from the primitive cell to model defects, surfaces, or phonons via finite differences. Example: A $3 \times 3 \times 3$ Si supercell contains 216 atoms for vacancy calculations. Practical application: Defect formation energies. Challenge: Finite-size effects and increased computational load.

Symmetry Operations – space group, point group – Transformations that leave the crystal invariant; QE automatically reduces k-point sets using symmetry. Example: The cubic Fm-3m space group reduces the irreducible Brillouin zone to 1/48 of the full zone. Practical application: Speeding up calculations. Challenge: Low-symmetry systems lose this advantage; manual symmetry input may be needed.

TDDFT – time-dependent DFT – Extension of DFT to excited-state dynamics; QE implements linear-response TDDFT for optical spectra. Example: Calculating the absorption spectrum of bulk silicon. Practical application: Optical property prediction. Challenge: Requires careful treatment of local-field effects and exchange-correlation kernels.

U-value – Hubbard parameter – The on-site Coulomb interaction strength used in DFT+U; can be computed via linear response or fitted to experiment. Example: Linear-response gives $U = 5.3$ eV for Fe-3d in FeO. Practical application: Improving magnetic moment predictions. Challenge: Dependence on the chosen projector and basis.

Van der Waals (vdW) Corrections – D2, D3, vdW-DF – Empirical or non-local functionals that add dispersion forces missing in semi-local DFT. Example: D3 correction reduces the interlayer distance of graphite from 3.5 Å (PBE) to 3.35 Å. Practical application: Layered materials and molecular adsorbates. Challenge: Selecting the appropriate scheme for a given system.

Wavefunction – $\psi_{nk}(r)$ – The Kohn-Sham orbital; expanded in plane-waves within QE. Example: Ψ_{nk} for a conduction band at the X point in Si. Practical application: Visualising orbital character. Challenge: Large data files; efficient I/O needed for post-processing.

Wannier Functions – maximally-localized – Real-space orbitals obtained from a unitary transformation of Bloch states; useful for interpolation of band structures and EPC. Example: Constructing Wannier90 files from QE outputs to interpolate the electron-phonon matrix of MgB₂. Practical application: High-resolution Fermi surfaces. Challenge: Disentanglement of bands and choice of initial projections.

XC Functional – exchange-correlation – Approximation for the many-body effects in DFT; includes LDA, GGA

(PBE, revPBE), meta-GGA, and hybrids. Example: PBE improves lattice constants over LDA for most metals. Practical application: Selecting a functional that balances accuracy and cost. Challenge: No universal functional; benchmarking is essential.

Zero-Point Energy (ZPE) – phonon ground-state energy – The quantum vibrational energy present at 0 K; can shift formation energies. Example: ZPE correction of ~ 0.05 eV for H₂ adsorption on Pt. Practical application: Accurate thermochemistry. Challenge: Requires full phonon calculations, increasing computational expense.

k-point Mesh – Monkhorst-Pack, Gamma-centered – The grid of reciprocal points used for Brillouin-zone integration; defined by three integers. Example: A $8 \times 8 \times 8$ Gamma-centered mesh for a cubic perovskite. Practical application: Systematic convergence studies. Challenge: Metallic systems often need denser meshes; non-orthogonal cells may require custom grids.

Linear-Response Theory – DFPT, susceptibility – Framework that computes the response of a system to a small perturbation without explicit supercells. Example: Calculating dielectric constants via "ph.X" linear-response. Practical application: Efficient phonon and EPC calculations. Challenge: Implementation limited to perturbations that preserve periodicity.

Magnetisation Density – $m(r)$ – Difference between spin-up and spin-down electron densities; visualisable to identify magnetic regions. Example: $M(r)$ shows localized moments on Mn atoms in MnO. Practical application: Designing spintronic devices. Challenge: Convergence of spin density can be slower than charge density.

Metadynamics – enhanced sampling – A technique to explore free-energy landscapes by adding bias potentials; can be coupled with QE via external drivers. Example: Metadynamics used to discover new Si polymorphs. Practical application: Overcoming kinetic barriers in structure prediction. Challenge: Choice of collective variables and bias parameters.

Non-Self-Consistent Field (NSCF) – band-structure run – A calculation that evaluates eigenvalues on a dense k-mesh using a fixed charge density from a preceding SCF. Example: NSCF run on a $24 \times 24 \times 24$ mesh to generate DOS. Practical application: High-resolution electronic spectra. Challenge: Must ensure the SCF density is fully converged.

Occupancy Smearing – degauss, smearing type – Parameter controlling the width of the smearing function; influences metallic SCF stability. Example: Degauss = 0.02 Ry for Al with Methfessel-Paxton smearing. Practical application: Reducing charge sloshing. Challenge: Too large a degauss artificially raises electronic temperature.

PAW Dataset – pseudopotential file – Contains atomic data for the PAW method; includes augmentation charges and projector functions. Example: Cu.Paw file includes 3d and 4s channels. Practical application: High-accuracy total-energy differences with moderate cutoffs. Challenge: Compatibility with specific XC functionals and hybrid calculations.

Projector Augmented-Wave (PAW) – all-electron reconstruction – Method that combines the efficiency of

pseudopotentials with the accuracy of all-electron calculations. Example: PAW reproduces core-level binding energies within 0.1 eV. Practical application: Reliable forces for transition-metal oxides. Challenge: Generating robust PAW datasets for rare-earth elements.

Quantum ESPRESSO (QE) Modules – pw.X, ph.X, cp.X, etc. – Individual executables each dedicated to a specific task: pw.X for ground-state DFT, ph.X for phonons, cp.X for Car-Parrinello MD, etc. Example: Running "pw.X -in scf.In > scf.Out" for an SCF calculation. Practical application: Modular workflow design. Challenge: Mastering the correct input syntax for each module.

Reciprocal Lattice – b_1, b_2, b_3 – Vectors defining the periodicity in k-space; used to generate k-point grids. Example: For a cubic lattice a , the reciprocal vectors have magnitude $2\pi/a$. Practical application: Constructing Brillouin-zone paths. Challenge: Low-symmetry cells may produce awkward reciprocal vectors, requiring custom mesh generation.

Relaxation Algorithm – CG, BFGS, FIRE – Numerical methods employed to minimise ionic forces; each has distinct convergence behaviour. Example: BFGS often converges faster for organic molecules than CG. Practical application: Efficient geometry optimisation. Challenge: Poor initial guesses can stall the optimizer; switching algorithms may help.

Self-Interaction Error (SIE) – DFT limitation – The spurious interaction of an electron with itself inherent to local and semi-local functionals, leading to delocalisation errors. Example: SIE causes underestimation of band gaps in ZnO. Practical application: Motivates use of hybrid functionals or DFT+U. Challenge: Quantifying SIE for a given system is non-trivial.

Spin-Polarised Calculation – collinear magnetism – DFT run where spin-up and spin-down electrons are treated separately, giving a net magnetic moment. Example: Setting "starting_magnetization(1)=0.5" for Fe in QE. Practical application: Modelling ferromagnets and antiferromagnets. Challenge: Convergence may be sensitive to the initial magnetisation and smearing.

Supercell Convergence – finite-size effects – The process of increasing the supercell size until defect formation energies or phonon frequencies no longer change significantly. Example: Vacancy formation energy in Si converges within 0.02 eV at a $3 \times 3 \times 3$ supercell. Practical application: Reliable defect energetics. Challenge: Computational cost grows rapidly with cell size.

Surface Slab Model – vacuum, dipole correction – A periodic slab representing a surface, separated by vacuum to avoid spurious interactions. Example: A 5-layer Si(111) slab with 15 Å vacuum. Practical application: Adsorption studies and work-function calculations. Challenge: Ensuring sufficient slab thickness and vacuum; dipole correction may be required for polar surfaces.

Symmetry-Reduced k-Points – irreducible Brillouin zone – The subset of k-points that, after applying symmetry operations, represent the full Brillouin zone. Example: A $6 \times 6 \times 6$ mesh reduces to 48 irreducible points for a cubic crystal. Practical application: Reducing computational effort. Challenge: Low symmetry leads to many irreducible points; manual symmetry specification may be needed.

Time-Step (MD) – Car-Parrinello, Born-Oppenheimer – The interval between successive updates of atomic

positions in molecular dynamics; determines accuracy and stability. Example: A 0.12 Fs time-step is typical for Car-Parrinello MD of water. Practical application: Simulating finite-temperature behaviour. Challenge: Too large a step leads to energy drift; too small increases cost.

Totally-Symmetric Representation – Γ representation – The irreducible representation that remains invariant under all symmetry operations; often used to label phonon modes at Γ . Example: The A_{1g} mode in Si belongs to the totally-symmetric representation. Practical application: Raman activity prediction. Challenge: Assigning correct representations for low-symmetry crystals.

Ultra-Soft Pseudopotentials (USPP) – Vanderbilt type – Pseudopotentials that allow lower cutoff energies by relaxing norm-conservation. Example: USPP for Ti reduces E_{cut} from 80 Ry (norm-conserving) to 40 Ry. Practical application: Large-scale simulations of transition-metal compounds. Challenge: May introduce ghost states if not carefully generated.

Van der Waals Density Functional (vdW-DF) – non-local correlation – An XC functional that includes a truly non-local term to capture dispersion interactions. Example: VdW-DF2 improves interlayer spacing of MoS_2 compared with PBE. Practical application: Layered heterostructures and physisorption. Challenge: Higher computational cost and occasional over-binding.

Wavefunction Cutoff – $ecutwfc$ – Parameter specifying the kinetic-energy cutoff for the plane-wave expansion of the Kohn-Sham orbitals. Example: $ecutwfc = 60$ Ry for Si leads to converged forces. Practical application: Primary convergence parameter. Challenge: Must be accompanied by a higher cutoff for charge density ($ecutrho \approx 4 \times ecutwfc$ for norm-conserving pseudopotentials).

Wannier90 Interface – post-processing tool – A code that reads QE outputs to construct maximally-localized Wannier functions and performs band interpolation. Example: Using "pw2wannier90.X" to generate input for Wannier90. Practical application: High-resolution band structures and electron-phonon coupling. Challenge: Selecting disentanglement windows; ensuring smooth gauge.

Zero-Temperature Approximation – static lattice – The assumption that nuclei are fixed at their equilibrium positions; neglects thermal vibrations. Example: DFT total energies are often reported at 0 K. Practical application: Baseline for formation-energy calculations. Challenge: ZPE and finite-temperature contributions may be non-negligible for light atoms.

k-point Weight – integration coefficient – The factor assigned to each irreducible k-point to correctly integrate over the Brillouin zone. Example: In a $4 \times 4 \times 4$ mesh, the Γ point may have weight = 1/64. Practical application: Accurate total-energy and DOS calculations. Challenge: Automatic weight generation may fail for distorted cells; manual correction sometimes needed.