Certificate in Quantum Espresso And VASP Theory

Band Structure And Dos

Antiferromagnetic Ordering – related terms: spin density, magnetic unit cell, exchange interaction. In a crystal where neighboring atomic spins align antiparallel, the net magnetisation cancels. Quantum Espresso implements antiferromagnetism through non-collinear spin calculations and the ‘nspin’ flag. VASP offers the ‘ISPIN=2’ and ‘LNONCOLLINEAR’ options to set up opposite spin sub-lattices. Example: Manganese oxide (MnO) exhibits type-II antiferromagnetism; a SCF run with a doubled magnetic cell reproduces the experimental band gap. Practical applications include spin-tronic devices where antiferromagnets provide fast switching and negligible stray fields. Challenges arise from the need for large super-cells, convergence of the magnetic moment, and the sensitivity of the exchange-correlation functional to the description of localized d-electrons.

Band Gap – related terms: direct gap, indirect gap, semiconductor, insulator. The band gap is the energy interval between the top of the valence band and the bottom of the conduction band where no electronic states exist. In Q-Espresso, the ‘bands.X’ post-processor extracts the gap from a calculated band structure; VASP reports the gap in the OUTCAR file. Example: Silicon has an indirect gap of ~1.1 EV; a DFT-PBE calculation underestimates it to ~0.6 EV, requiring a hybrid functional (HSE06) or GW correction for quantitative accuracy. Band-gap engineering underpins optoelectronic devices such as LEDs and solar cells. The main challenge is the systematic underestimation of gaps by semi-local functionals, which demands more expensive many-body methods or empirical scissor operators.

Band Structure – related terms: Brillouin zone path, high-symmetry points, dispersion, effective mass. A band structure is a plot of electronic eigenvalues versus crystal momentum along a prescribed path through reciprocal space. In Quantum Espresso the workflow typically involves a SCF run, a non-SCF calculation on a dense k-mesh, and the ‘bands.X’ utility to generate eigenvalues; VASP uses the ‘KPOINTS’ file with a line-mode list. Example: Graphene’s linear dispersion near the K point yields massless Dirac fermions, observable as a characteristic “cone” in the calculated band plot. Band structures guide material selection for transistors, thermoelectrics, and superconductors. Challenges include selecting an appropriate k-path that respects crystal symmetry, converging the calculation for metallic systems, and interpreting band crossings that may be artefacts of the chosen exchange-correlation approximation.

Brillouin Zone – related terms: Reciprocal lattice, primitive cell, symmetry points. The Brillouin zone (BZ) is the Wigner-Seitz cell of the reciprocal lattice; it contains all distinct k-vectors required to describe the periodic electronic structure. Both Q-Espresso and VASP generate the BZ automatically from the lattice vectors supplied in the input. Example: For a face-centered cubic lattice, the BZ is a truncated octahedron with high-symmetry points Γ, X, L, and W. The BZ is the domain for k-point sampling, and its geometry determines the density of states near critical points. Practical use includes selecting k-paths that pass through symmetry points for band-structure plots. A common difficulty is handling low-symmetry or incommensurate structures where the BZ shape is complex, requiring careful generation of a uniform Monkhorst-Pack grid or a custom k-mesh.

Bloch Theorem – related terms: Bloch functions, periodic boundary conditions, crystal momentum. Bloch's theorem states that electronic wavefunctions in a periodic potential can be written as a plane wave multiplied by a lattice-periodic function: Ψk(r)=e^{ik·r}uk(r). This theorem is the foundation of plane-wave DFT codes such as Quantum Espresso and VASP, allowing the use of a finite basis set despite the infinite crystal. Example: The plane-wave expansion of uk(r) is truncated by a kinetic-energy cutoff; increasing the cutoff improves accuracy at the cost of CPU time. Bloch theorem enables the calculation of band structures, DOS, and response functions. The main challenge lies in representing strongly localized states (e.G., 3D orbitals) with plane waves, often mitigated by employing pseudopotentials or projector-augmented wave (PAW) methods.

Density of States (DOS) – related terms: partial DOS, smearing, Fermi level. The DOS, g(E), counts the number of electronic states per energy interval; it is obtained by integrating the band structure over the Brillouin zone. In Quantum Espresso the 'dos.X' utility processes eigenvalues to produce total and projected DOS; VASP provides the 'DOSCAR' file. Example: A metallic system such as copper shows a finite DOS at the Fermi level, whereas an insulator like MgO displays a gap where g(E)=0. DOS analysis assists in identifying orbital contributions to bonding, assessing metallicity, and estimating carrier concentrations. Challenges include choosing an appropriate smearing width to avoid artificial oscillations, and ensuring sufficient k-point density for convergence, especially near van Hove singularities.

Fermi Level – related terms: Chemical potential, occupancy, metallicity. The Fermi level (EF) is the energy at which the probability of occupation is ½ at zero temperature; in DFT it is set by the total electron count and the chosen smearing scheme. Both Q-Espresso and VASP output EF after a SCF cycle; it serves as the reference for aligning band structures and DOS plots. Example: For a doped semiconductor, the Fermi level shifts into the conduction band, indicating n-type behavior. Applications include determining carrier type, designing Schottky contacts, and evaluating thermoelectric performance via the Seebeck coefficient. The main difficulty is the dependence of EF on the smearing method (e.G., Methfessel–Paxton vs. Gaussian), which can affect the apparent metallicity of borderline systems.

Fermi Surface – related terms: nesting vector, electron pocket, hole pocket. The Fermi surface is the constant-energy manifold in k-space where the band energy equals the Fermi level. It can be visualized using the 'fermi_surface.X' tool in Quantum Espresso or the 'FSX' post-processor in VASP. Example: In the high-temperature superconductor $BaFe_2As_2$, the Fermi surface consists of quasi-two-dimensional electron and hole cylinders that are linked by a nesting vector, promoting spin-density-wave order. Fermi-surface topology influences transport properties, superconductivity, and magnetic instabilities. Challenges include achieving fine k-mesh resolution to capture small pockets, handling spin-orbit splitting, and integrating over complex surfaces without introducing numerical noise.

Gamma Point – related terms: Zone centre, k=0, symmetry. The Γ point (k = 0) is the centre of the Brillouin zone where the crystal momentum vanishes. It is often included in k-point grids to capture the zone-center electronic states. In VASP a Γ-centered Monkhorst-Pack grid is specified with 'Gamma-centered'; Quantum Espresso uses the 'gamma' keyword. Example: Phonon calculations at the Γ point provide the acoustic mode frequencies, essential for evaluating lattice stability. The Γ point is crucial for optical spectroscopy, where transitions often involve zone-center states. A practical issue is that Γ-only calculations

can miss dispersion effects, leading to inaccurate total energies for metallic systems; therefore a denser k-mesh is recommended.

K-point Sampling – related terms: Monkhorst-Pack grid, convergence, symmetry reduction. K-point sampling defines the discrete set of reciprocal-space points used to approximate Brillouin-zone integrals. The Monkhorst-Pack scheme generates a uniform grid (e.G., 6 × 6 × 6) That respects crystal symmetry; both Q-Espresso ('K_POINTS automatic') and VASP ('KPOINTS') support it. Example: A convergence test for silicon shows that a 8 × 8 × 8 grid yields total-energy differences below 1 meV per atom compared with a 10 × 10 × 10 grid. Adequate k-sampling is essential for accurate band structures, DOS, and forces. Challenges include balancing computational cost against accuracy, especially for large super-cells where the Brillouin zone shrinks and fewer k-points may be sufficient, and handling metallic smearing to avoid convergence stalls.

Lattice Constant – related terms: Equilibrium geometry, cell optimization, stress tensor. The lattice constant is the length of the primitive translation vectors that define the periodic cell. In DFT calculations the lattice constant is optimized by minimizing the total energy with respect to cell parameters; Quantum Espresso uses the 'vc-relax' calculation type, while VASP employs 'ISIF=3'. Example: The experimental lattice constant of bulk aluminum is 4.05 Å; a PBE calculation yields 4.07 Å, demonstrating typical GGA overestimation. Accurate lattice constants are prerequisite for reliable band-structure predictions, as small changes can shift band edges and modify the band gap. Difficulties arise from the choice of exchange-correlation functional, the presence of van der Waals interactions, and the need for high-precision convergence criteria for forces and stresses.

Muffin-Tin Potential – related terms: APW method, sphere radius, interstitial region. The muffin-tin approximation partitions space into non-overlapping atomic spheres (the "tin") and an interstitial region where the potential is assumed constant. While not directly used in plane-wave codes, the concept underlies all-electron methods such as the linearized augmented plane-wave (LAPW) approach, which can be interfaced with VASP-PAW for benchmarking. Example: In Fe-based superconductors, a small muffin-tin radius may exclude important d-electron density, leading to errors in magnetic moment calculations. Understanding muffin-tin concepts helps users interpret differences between PAW and full-potential results. The challenge is selecting sphere radii that avoid overlap while capturing enough charge, a task that becomes non-trivial for low-symmetry or highly distorted structures.

Pseudopotential – related terms: PAW, norm-conserving, ultrasoft, core electrons. A pseudopotential replaces the all-electron potential with a smoother effective potential that reproduces valence-electron behavior while eliminating the need to treat core states explicitly. Quantum Espresso uses norm-conserving or ultrasoft pseudopotentials (UPF format); VASP employs the PAW method, which can be viewed as a generalized pseudopotential. Example: A GGA-PBE pseudopotential for silicon reproduces the experimental lattice constant within 1 %; however, a poorly constructed pseudopotential may give spurious band-gap values. Pseudopotentials enable tractable plane-wave calculations for large systems, surface slabs, and molecular dynamics. Challenges include ensuring transferability across oxidation states, handling semi-core states, and verifying that the chosen potential reproduces reference all-electron data for the property of interest.

Quasiparticle – related terms: GW approximation, self-energy, band-gap renormalization. In many-body theory a quasiparticle is an electron (or hole) dressed by its interaction with the surrounding electronic cloud, characterised by an energy-dependent self-energy Σ(k, E). The GW method, often applied as a post-processing step after a DFT run, corrects the Kohn-Sham eigenvalues to quasiparticle energies. Example: Applying G_0W_0 to bulk silicon raises the PBE band gap from 0.6 EV to ~1.2 EV, close to the experimental value. Quasiparticle calculations are essential for accurate optical spectra, band-alignment studies, and defect level predictions. The main difficulties are the high computational cost, the sensitivity to the starting DFT functional, and the need for a dense k-mesh and many empty bands to achieve convergence.

Reciprocal Space – related terms: Fourier transform, G-vectors, Brillouin zone. Reciprocal space is the Fourier-conjugate of real space, where periodic functions are expressed as sums over plane waves with wavevectors G. In plane-wave DFT, the kinetic-energy cutoff determines the maximum |G| included. Both Q-Espresso and VASP operate primarily in reciprocal space, converting ionic potentials to G-space via FFT. Example: increasing the cutoff from 30 Ry to 50 Ry for a transition-metal oxide improves the description of localized d-states but raises CPU time. Reciprocal-space representation simplifies the evaluation of the Hartree and exchange-correlation energies. Challenges include memory consumption for large cutoffs, aliasing errors when the grid is insufficient, and handling non-periodic boundary conditions in slab or cluster calculations.

Self-Consistent Field (SCF) – related terms: Charge density, convergence tolerance, mixing scheme. An SCF cycle iteratively solves the Kohn-Sham equations until the input and output charge densities agree within a predefined tolerance. Quantum Espresso invokes 'pw.X' with 'calculation = scf'; VASP uses the 'IBRION = -1' flag to perform an electronic minimisation only. Example: A metallic system may require a smearing scheme (e.G., 'Methfessel-Paxton 1') and a mixing parameter of 0.3 To achieve convergence within 10^{-6} Ry. SCF convergence is a prerequisite for reliable forces, total energies, and derived properties such as band structures. Common challenges include charge sloshing in large cells, slow convergence for systems with flat bands, and the need for preconditioning or advanced mixing algorithms (e.G., Broyden).

Spin-Orbit Coupling – related terms: Relativistic effects, band splitting, topological insulator. Spin-orbit coupling (SOC) arises from the interaction between an electron's spin and its orbital motion, leading to band splitting especially in heavy elements. In VASP SOC is activated with 'LSORBIT = .TRUE.' and a non-collinear magnetisation; Quantum Espresso includes SOC via the 'noncolin' and 'lspinorb' flags. Example: Bismuth selenide (Bi_2Se_3) exhibits a surface Dirac cone only when SOC is included; neglecting SOC predicts a trivial band ordering. SOC is essential for designing spintronic materials, Rashba devices, and topological phases. The computational cost roughly doubles due to the need for spinor wavefunctions, and convergence may require finer k-meshes. Additionally, pseudopotentials must be generated with SOC included to avoid inconsistencies.

Tight-Binding Model – related terms: Hopping parameters, Wannier functions, band interpolation. The tight-binding (TB) approach approximates the electronic structure by a set of localized orbitals with hopping integrals between them. It provides a bridge between first-principles DFT results and analytical models. Example: Constructing a TB Hamiltonian for graphene from maximally localized Wannier functions

reproduces the linear Dirac dispersion with only nearest-neighbour hopping. TB models are widely used for rapid evaluation of transport, topological invariants, and large-scale simulations where full DFT is prohibitive. Challenges include accurately extracting hopping parameters from DFT (requiring Wannierisation), handling long-range interactions, and ensuring that the model respects crystal symmetry.

Van Hove Singularity – related terms: DOS peak, saddle point, electronic instability. A van Hove singularity occurs when the band dispersion has a saddle point, causing a logarithmic divergence in the DOS. In a two-dimensional material, this manifests as a pronounced DOS peak. Example: The cuprate superconductor $La_{2-x}Sr_xCuO_4$ shows a van Hove singularity near the Fermi level at optimal doping, which is believed to enhance superconductivity. Identifying van Hove singularities helps in tuning electronic properties via strain or doping. The challenge lies in resolving the singularity, which requires extremely fine k-point sampling and careful smearing choices to avoid artificial broadening.

Wannier Functions – related terms: Localization, MLWF, band disentanglement. Wannier functions are real-space orbitals obtained by unitary transformation of Bloch states, providing a compact representation of the electronic structure. Maximally localized Wannier functions (MLWF) are constructed through an iterative minimisation of spread; the ‘wannier90’ code interfaces with both Quantum Espresso and VASP. Example: Generating MLWF for the d-orbitals of a transition-metal oxide enables the construction of an accurate TB model for many-body calculations such as dynamical mean-field theory (DMFT). Wannier functions facilitate interpolation of band structures on ultra-dense k-grids, calculation of Berry phases, and modeling of electron-phonon coupling. Difficulties arise when the target bands are entangled with higher-energy states, requiring careful selection of energy windows and disentanglement procedures to obtain physically meaningful Wannier functions.