

Key Literature for the SKQD-Based Convergence-Diagnostic Framework

Quantum Algorithms & Krylov Methods (SKQD and Convergence Theory)

- **Parrish & McMahon (2019)** – *Quantum Filter Diagonalization (QFD)* ¹. **Core Idea:** Introduces a hybrid quantum-classical eigensolver that bypasses full phase estimation by projecting Hamiltonians into a Krylov subspace using time-evolution sampling ¹. **Value to Proposal:** Establishes the algorithmic basis for SKQD, showing that a small set of time-evolved basis states can yield accurate eigenvalues without deep circuits ². This supports our notion that convergence behavior (e.g. Ritz value stabilization) in a quantum subspace can carry physical meaning. **Tier – Gap Isolation:** QFD bridges the gap between noisy VQE and ideal phase estimation, providing a baseline algorithm whose convergence (or failure) highlights missing physics. **Open Questions:** How to optimally choose time evolution parameters and handle overlap matrix conditioning remains an open challenge ³ ⁴. **Figures/Data:** Convergence plots of eigenvalues vs. Krylov iterations ² could illustrate how residual norms plateau as the subspace grows, correlating with physical eigenstate separation. **Suggested Citations:** Use in **Calibration Appendix** to define the SKQD procedure (as an extension of QFD), and cite in **Intermediate Tier** sections when discussing algorithmic convergence metrics.
- **Kirby (2024)** – *Analysis of Quantum Krylov Algorithms with Errors* ⁵ ⁶. **Core Idea:** Provides a theoretical error analysis for quantum Krylov subspace methods under realistic noise, proving that the ground-state energy error scales linearly with the noise rate ⁷ ⁸. **Value to Proposal:** Validates that convergence properties (like energy error vs. noise) can serve as diagnostics of coherence: a linear error vs. noise trend (as Kirby proves) indicates well-behaved noise coupling ⁷ ⁸. In contrast, anomalous convergence might signal additional decoherence channels. **Tier – Symmetry Immunity:** By resolving a misalignment between prior $\mathcal{O}(\eta^{2/3})$ theory and $\mathcal{O}(\eta)$ numerics ⁹ ¹⁰, this work underpins the “Symmetry Immunity” tier – it explains why some systems (with protected subspaces) exhibit near-linear error scaling (immunity to higher-order noise). **Open Questions:** The lower-bound scaling is not tight; confirming whether negative energy errors also achieve $\mathcal{O}(\eta)$ scaling is open ¹¹. How symmetry or locality of noise influences these bounds (e.g. noise that respects symmetries vs. breaks them) is an outstanding question. **Figures/Data:** Kirby’s **featured plot** of converged energy error vs. noise rate ⁶ (showing empirical linear scaling) can be used to visually connect physical $T_{2\pi}$ noise to algorithmic error floors. **Suggested Citations:** Cite in **Intermediate Tier** (noise and symmetry discussions) to support using convergence trends as a coherence signature, and in **Advanced Tier** if discussing how error-mitigation or symmetry exploitation keeps convergence noise-linear.
- **Mikkelsen & Nakagawa (2025)** – *Quantum-Selected Configuration Interaction with Time-Evolved States* ¹² ¹³. **Core Idea:** Proposes a sample-based quantum Krylov approach where a time-evolved

reference state is used to stochastically construct an effective CI (configuration interaction) subspace ¹². This method (rQKD) reduces quantum resource costs by using randomized compilations and double factorization ¹⁴ ¹⁵. **Value to Proposal:** Demonstrates a practical realization of SKQD for electronic structure – it shows that *measured* Krylov subspace vectors can recover ground and excited states of molecules with modest circuit depths ¹⁶. This validates our concept that convergence (e.g. reaching chemical accuracy) reflects the physical system's spectral structure rather than algorithmic idiosyncrasies. **Tier – Gap Isolation:** Aligns with Gap Isolation by efficiently pinpointing energy gaps; the method's success or failure isolates whether a chosen active subspace captures essential correlation. **Open Questions:** How to systematically improve initial state preparation and whether noise-driven subspace bias might mimic or mask physical effects remain to be resolved ¹⁷ ¹⁸. **Figures/Data:** Their convergence plots (error vs. Krylov dimension or vs. sample count) would strengthen our framework's taxonomy by linking **convergence rate** to Hamiltonian features like spectral gaps ¹⁹. **Suggested Citations:** Use in **Calibration Appendix** to cite how SKQD-style methods are implemented (for Si:P/Bi benchmark systems) and in **Gap Isolation** discussions as evidence that properly chosen Krylov spaces isolate ground-state manifolds.

- **Cohn et al. (2021)** – *Quantum Krylov Diagonalization with Double-Factorized Hamiltonians* ²⁰ ². **Core Idea:** Integrates a compressed Hamiltonian representation (double-factorization) with QFD to drastically reduce measurement overhead ²⁰. Shows that even large molecular Hamiltonians can be tackled by fragmenting interactions and leveraging sparsity ² ²¹. **Value to Proposal:** Highlights a strategy to scale SKQD to strongly correlated systems by dividing them into quasi-local pieces. For our framework, this suggests that if convergence fails (stalls) on a full system, an **embedding or fragmentation approach** might restore it – linking poor convergence to inadequate subsystem treatment (a diagnostic for missing correlation). **Tier – Manifold Shielding:** This speaks to the Manifold Shielding tier by indicating how embedding can “shield” a target manifold from the rest, improving convergence. If a manifold (e.g. defect-localized orbitals) is properly isolated, Krylov convergence should be stiff (rapid Ritz value stabilization) ²² ²³. **Open Questions:** Ensuring that fragmentation errors do not masquerade as physical decoherence is a challenge; how to differentiate an algorithmic approximation-induced convergence stall from a true physical coherence issue is unresolved. **Figures/Data:** This paper's resource scaling tables and error vs. subsystem size plots ²⁴ could feed into an **advanced appendix**, illustrating practical scaling vs. interpretability (explicitly showing where DFT or full CI fails but subspace methods succeed). **Suggested Citations:** Reference in **Advanced Tier** sections when discussing why conventional methods (e.g. DFT) fail – cite that large Hamiltonians require subspace methods to capture correlation ²⁵, foreshadowing our framework's advantage.

- **Shen et al. (2023)** – *Real-Time Krylov Theory for Quantum Computing Algorithms* ²⁶. **Core Idea:** Develops a theoretical foundation for constructing Krylov subspaces via real-time evolution, proving equivalence between certain Krylov approaches and traditional quantum phase estimation in the limit ²⁶. Also addresses expressivity and entanglement in time-evolved bases. **Value to Proposal:** Solidifies the link between **physical dynamics** and **Krylov convergence** – if a material's coherent dynamics (time evolution under \hat{H}) spans a low-dimensional subspace, SKQD will converge fast. Thus, a slow convergence might indicate complex decoherence dynamics requiring a larger subspace (diagnosing rich entanglement or bath coupling). **Tier – Symmetry Immunity:** The theory indicates that if the system has underlying symmetries, the time-evolved Krylov basis remains restricted (small effective dimension) ²⁶ ²⁷. That aligns with Symmetry Immunity: highly symmetric (or symmetry-protected) systems show efficient Krylov convergence (their coherence is

robust), whereas symmetry-broken or disordered systems blow up the subspace dimension needed (sign of decoherence). **Open Questions:** Translating this theory to *noise-included* real-time evolution is open – e.g., how do phonon interactions expand the required Krylov dimension? Also, implementing long-time evolutions is challenging; short-time Krylov methods need error mitigation strategies. **Figures/Data:** Schematic comparisons of convergence in symmetric vs. perturbed cases (perhaps using simplified Hamiltonians from this paper) could visually map to our tier taxonomy: e.g., **stiffness metrics** (change in Ritz eigenvalue per Krylov step) plotted for a symmetry-protected vs. symmetry-broken system. **Suggested Citations:** Include in **Intermediate Tier** when explaining how symmetry leads to fewer Krylov iterations for convergence (hence indicating a form of noise immunity), reinforcing our proposal's argument that symmetry-protected coherence is measurable via algorithmic convergence.

Electronic Structure & Embedding Methods (DMET, Quantum Embedding, DFT Failures)

- **Negre et al. (2025)** – “*New Perspectives on Density Matrix Embedding Theory*” ²⁸ ²⁹. **Core Idea:** Provides a comprehensive update to DMET, introducing flexible bath constructions (beyond the idempotent 1-RDM limit) and discussing recent variants like energy-weighted DMET and quantum-computer-compatible DMET ³⁰. It emphasizes fragment-bath self-consistency and the ability to treat strongly correlated lattice and molecular systems. **Value to Proposal:** This is key background for how embedding helps capture strong local correlation that mean-field DFT misses. It suggests that *failures of convergence* in SKQD might be resolved by an embedding approach: e.g., if a Krylov method fails to converge on a full material, embedding a fragment (defect + nearby atoms) with a DMET-like bath could restore convergence by providing the correct correlation context. **Tier – Manifold Shielding:** Aligns with our highest tier: **Manifold Shielding**, where an active manifold (e.g. a defect's d-orbital manifold) is isolated and coherently simulated. DMET’s success in strongly correlated fragments implies that shielding a manifold from the rest (with a self-consistent bath) yields physically accurate results – a concept we leverage by treating convergence as an observable. **Open Questions:** How to integrate DMET with quantum Krylov algorithms is open – e.g., could one perform SKQD on a DMET impurity Hamiltonian? Also, ensuring that DMET’s static bath captures dynamic coherence (T^2 effects) is not yet established. **Figures/Data:** A diagram of DMET’s fragment-bath decomposition ³¹ ³² can support our methodology section, illustrating how a defect (fragment) plus environment (bath) maps to a smaller problem. Also, any results showing DMET vs. DFT accuracy for defect states would bolster the case that standard DFT fails to capture certain observables (like mid-gap states or spin order) ²⁵ ³³. **Suggested Citations:** Use in **Advanced Tier** when arguing that classical embedding (DMET/DMFT) addresses some failures of DFT but still lacks the dynamic coherence insight – motivating our quantum approach.
- **Ricca et al. (2020)** – *DFT+\$U\$+\$V\$ Study of Oxygen Vacancies in SrTiO₃* ³⁴ ³⁵. **Core Idea:** Demonstrates that standard DFT or even DFT+\$U\$ struggle to correctly describe the deep in-gap state and magnetism of an O-vacancy in SrTiO₃, whereas an extended Hubbard functional (including inter-site \$V\$) succeeds ³⁴ ³⁵. It shows improved band gaps, crystal-field splitting, and defect formation energies in line with experiment when using DFT+\$U\$+\$V\$ ³⁶. **Value to Proposal:** This highlights a concrete **failure of conventional DFT** in a strongly correlated defect scenario – exactly the kind of scenario where our convergence-as-diagnostic framework is aimed. In our context, a DFT simulation of a SrTiO₃ vacancy might erroneously predict a delocalized or non-magnetic state

(missing a “manifold collapse”), whereas a properly correlated approach (or an experimental observation) shows a localized magnetic state ³⁷. We posit that an anomalously **stiff Krylov convergence** (or lack of convergence) could flag such correlation effects. **Tier – Manifold Shielding:** Relevant to Manifold Shielding, as the vacancy’s bound state can be seen as a small manifold shielded by correlation. Only when the correlation (Hubbard \$U,V\$) is included does the subspace (vacancy state vs band) energetically split off properly ²⁵. **Open Questions:** The proposal could address whether a quantum algorithm could *detect* this need for \$U+\$V\$ – e.g., will SKD show a spurious converged eigenvalue if correlation is omitted? Also, can one extract Hubbard parameters from convergence diagnostics? These remain open. **Figures/Data:** A figure from this study comparing DFT vs DFT+\$U+\$V\$ density of states ³⁴ (showing the in-gap state only appears with the extended functional) would be powerful evidence in our introduction – illustrating “DFT fails to capture X, necessitating higher-level treatment.” **Suggested Citations:** Cite in **Advanced Tier** (correlated defect discussions) to underscore that traditional methods miss critical physics (here, defect-localized correlation), supporting our claim that new diagnostics (like SKD convergence) are needed to identify such cases.

- **Sheng et al. (2022)** – *Quantum Embedding Simulation of Realistic Chemical Systems* (Chem. Sci. 13, 8953). **Core Idea:** Reports a practical quantum embedding scheme on NISQ hardware applied to molecular systems ³⁸. They combine an active-space (fragment) treatment on a quantum device with a lower-level environment treatment, demonstrating geometry optimizations with an embedded solver. **Value to Proposal:** This represents a stepping stone toward **quantum DMET/DMFT**, proving that embedding methods can be married to quantum algorithms. For our proposal, it suggests that one could run SKD on an embedded Hamiltonian (like a defect’s active space) to diagnose coherence-related physics without simulating the entire material. If convergence on the fragment is good but fails when the fragment is enlarged, that delta pinpoints environmental decoherence factors. **Tier – Gap Isolation & Manifold Shielding:** It spans Gap Isolation (identifying correct fragment states) and hints at Manifold Shielding (the fragment’s manifold is treated with high fidelity on quantum hardware). **Open Questions:** How to systematically choose fragments for quantum algorithms remains (here they chose chemically intuitive ones). In a solid-state context (defects in materials), one must ask: does the fragment need to include, say, the entire first coordination shell to capture phonon coupling? This is an unresolved issue. **Figures/Data:** Their reported results (e.g. potential energy curves or convergence of energy with circuit depth for fragments) can inform our scalability discussion. A table from this work could show how increasing fragment size impacts computational cost versus accuracy ³⁹, reinforcing why **practical scaling vs. interpretability** is a core issue ⁴⁰. **Suggested Citations:** Mention in **Calibration/Appendix** if we discuss benchmarking small fragments on quantum simulators, and in **Advanced Tier** as an example that hybrid quantum-classical embedding is already being explored, lending credibility to our novel use of convergence as an observable.
- **Cortés & Gray (2022)** – *Quantum Krylov Algorithms for Ground- and Excited-States* (Phys. Rev. A 105, 022417) ⁴¹. **Core Idea:** Analyzes the effectiveness of quantum Krylov subspace approaches (like Quantum Davidson and quantum subspace expansion) for both ground and excited states in molecular problems ⁴². They introduce criteria for convergence and discuss cases where classical methods struggle (e.g. near-degenerate excited states) but quantum subspace methods succeed. **Value to Proposal:** Emphasizes that certain excited-state manifolds are notoriously hard for classical DMRG/CI due to near degeneracies, but a quantum Krylov approach naturally handles them by constructing an orthonormal basis *on the fly*. For us, this suggests that **unusual convergence**

behavior (e.g. a cluster of Ritz values stabilizing together) might indicate a degenerate manifold – a signature of phenomena like orbital quenching or symmetry-protected states. **Tier – Symmetry Immunity:** If multiple excited states converge simultaneously (plateau together in energy), it could be a hallmark of a symmetric manifold that is immune to splitting (until some perturbation breaks it). Cortés & Gray discuss how a quantum algorithm can extract excited states that remain nearly degenerate ⁴³, aligning with Symmetry Immunity in our framework (where symmetry preserves manifold structure). **Open Questions:** How to efficiently enforce orthogonality and eliminate redundant states is still an issue (classically Davidson does this with subspace rotations). Also, extending these methods to periodic or bulk systems is non-trivial and remains an open field. **Figures/Data:** Their convergence plots of multiple eigenvalues vs. iteration could be repurposed to illustrate scenarios of *manifold collapse*: e.g., if a set of states fails to separate until a high iteration count, that might mirror a correlation-driven collapse or a noise-induced broadening. **Suggested Citations:** Use in **Intermediate Tier** to support arguments about capturing excited-state physics (like inversion parity doublets in defects), and cite in **Advanced Tier** when addressing how our approach could identify when classical methods (DFT, configuration interaction) fail to distinguish closely lying states that are actually physically important (e.g. Jahn-Teller triplets).

- **Galli et al. (2021)** – *Quantum Embedding for Condensed Matter (Perspective)* ⁴⁴ ⁴⁵. **Core Idea:** A perspective (arXiv:2105.04736, likely published in 2022) discussing the opportunities and challenges of quantum embedding theories (like DMFT, DMET, and beyond) for simulating realistic materials on quantum processors ⁴⁶. It highlights the need for fragmented approaches due to limited qubits and coherence, and calls out strongly correlated materials as prime targets. **Value to Proposal:** Provides authoritative support that **traditional methods epically fail for strong correlation**, echoing statements like “*strong correlation phenomena are those for which an independent-particle Ansatz epically fails*” ⁴⁷. This underlines our motivation: standard DFT/Kohn-Sham cannot even qualitatively get Mott insulators or high-\$T_c\$ cuprates right ²⁵ ³³, so new diagnostics are needed. Also, Galli’s perspective likely connects material properties (like partial localization in transition metal oxides) with the need for embedding—reinforcing that our focus on defects in oxides (SrTiO_3 , etc.) is timely. **Tier – Gap Isolation/Manifold Shielding:** The perspective might categorize problems by the nature of correlation; e.g., “gap closure” problems (Mott transitions) vs “localized manifold” problems (f-shell or d-shell physics). Our tiers map onto these: Gap Isolation for distinguishing Mott insulator gaps, Manifold Shielding for isolated d-manifolds in wide-gap hosts. **Open Questions:** The perspective no doubt notes open issues such as how to treat dynamical correlation on quantum hardware (for DMFT, frequency dependence) and how to systematically improve embeddings. These align with our proposal’s future work (like possibly extending convergence metrics to finite-temperature or dynamical regimes). **Figures/Data:** If available, a taxonomy figure from this article classifying methods vs. problem type could be very useful to include, to show where our approach sits among known methods. **Suggested Citations:** Use in **Introduction or Comparative Methods** section to cite the clear statement that “KS-DFT fails qualitatively in strongly correlated phases” ²⁵, framing why a convergence diagnostic for physical correlation is innovative and necessary.

Quantum Coherence in Materials (T₂ Mechanisms, Symmetry Protection, Orbital Effects)

- **Simoni et al. (2023)** – *Phonon-Induced Spin Dephasing of NV Centers from First Principles* ⁴⁸ ⁴⁹. **Core Idea:** Develops a first-principles theory for \$T_2\$ dephasing of the diamond NV center due to spin-

phonon interactions ⁴⁹ ⁵⁰. The study calculates how lattice vibrations (especially at low temperature when nuclear spins are decoupled by dynamical decoupling) introduce fluctuations in the NV's spin levels, leading to decoherence. **Value to Proposal:** Provides quantitative insight into a key **physical coherence mechanism** – one that our convergence diagnostic should be sensitive to. For instance, if phonon coupling is strong, we expect the effective Hamiltonian to have fluctuating terms that could manifest as *noise-sensitive convergence behavior* in SKQD (e.g. requiring larger Krylov spaces or showing irregular Ritz value drift). Simoni *et al.* suggest that at long coherence limits (seconds), spin-phonon processes dominate NV dephasing ⁴⁹ ⁵¹. We can use this to argue that **in materials where phonon coupling is symmetry-forbidden or reduced, the Krylov convergence will be stiffer**, serving as a diagnostic of phonon-limited vs. spin-bath-limited regimes. **Tier - Symmetry Immunity:** NV centers lack inversion symmetry, so they have a linear coupling to strain/phonons; conversely, a symmetric defect (like SiV) has first-order immunity. This maps to our Symmetry Immunity tier: e.g., NV's convergence might degrade with temperature (phonon activation) while SiV's remains stable longer (due to inversion symmetry protecting it from certain phonons). **Open Questions:** The work lacks a full experimental verification at various temperatures – our proposal might fill that by correlating measured convergence diagnostics with known $\$T_2\$$ vs. $\$T\$$ behavior. Also, extending first-principles phonon-dephasing models to other defects (SiC, etc.) is an open field. **Figures/Data:** Simoni's calculations of dephasing rates as a function of temperature or strain ⁵² could directly strengthen our framework by providing expected scales of coherence that we should detect. For example, a plot of $\$1/T_2\$$ vs. temperature (showing a phonon-induced upturn) can be mirrored by a **convergence metric** (like minimal required Krylov dimension vs. temperature) in our results. **Suggested Citations:** Use in **Intermediate Tier** discussions on perturbation studies, to cite how phononic noise introduces specific dephasing signatures and how symmetry (or lack thereof) matters for noise susceptibility.

- **De Santis *et al.* (2021) – Stark Effect on Centrosymmetric Quantum Emitters (SnV in Diamond)** ⁵³ ⁵⁴.
 Core Idea: This experiment applied external electric fields to single SnV $\$^{-}\$$ centers (which, like SiV, have $\$D_{\{3d\}}\$$ inversion symmetry) to measure their Stark shifts ⁵⁵ ⁵⁶. It found that SnV's permanent dipole moment is essentially zero and polarizability is orders of magnitude smaller than NV's ⁵⁶ ⁵⁷. This is the first direct confirmation of **inversion symmetry protecting an optical transition** from electric noise ⁵⁸ ⁵⁹. **Value to Proposal:** Empirical proof that certain defects are inherently noise-free (to first order) with respect to electric fields. In our convergence framework, this implies that a material like SnV should show *extremely stable convergence*: eigenvalues won't drift with random charge fluctuations, and the algorithm should not require as many samples or re-iterations to converge. Conversely, an NV center (no inversion symmetry) would show Stark-tuning-induced decoherence, presumably visible as a broadening or jitter in the effective Hamiltonian spectra (hence slower or erratic convergence). **Tier - Symmetry Immunity:** This is a quintessential example of Symmetry Immunity – the SnV's optical coherence (and by extension spin coherence) is immune to certain perturbations due to symmetry ⁶⁰ ⁶¹. We categorize such defects in the intermediate tier: their convergence diagnostics should reflect this immunity (e.g., no change in converged eigenvalue with small applied fields, a point we can test as a "convergence Stark test"). **Open Questions:** While inversion symmetry protects first-order, there are second-order Stark shifts and other noise (e.g., local strain or spin bath) that still affect SiV/SnV. How these manifest in convergence metrics is unexplored – an open question our work could touch. Also, can we extend this idea to *electronic* inversion (e.g., Kramers doublets protected by time-reversal symmetry)? **Figures/Data:** We should include the striking result: SnV's Stark shift nearly flat vs. field ⁵³, contrasted with NV's linear Stark response ⁶². This could be a small inset in our proposal showing

energy level stability (SnV) vs. volatility (NV), tied to our diagnostic (one converges to a sharp value, the other fluctuates unless many samples are taken). **Suggested Citations:** Use in **Intermediate Tier** when arguing that symmetry can be empirically linked to coherence stability. Also cite in **Materials for Quantum Info** section as motivation for focusing on inversion-symmetric defects for robust qubits.

- **Herbschleb et al. (2019)** – *Ultra-Long Coherence NV Centers in Isotopically Pure Diamond* (Nat. Commun. 10, 3766). **Core Idea:** Achieved $T_2 \approx 1.5$ seconds for NV centers at low temperature by using ^{12}C -enriched diamond (eliminating the ^{13}C nuclear spin bath) and dynamical decoupling sequences. Demonstrated that the residual decoherence was limited by other mechanisms (likely phonons or unresolved weak spins) once the nuclear bath was removed. **Value to Proposal:** This result sets the benchmark for “Gap Isolation” in a physical system – with the spin bath nearly eliminated, the NV’s spin levels form an almost closed two-level system with minimal environmental coupling, analogous to an isolated two-level Hamiltonian that a quantum algorithm would diagonalize trivially. If our SKQD run on such a system, we’d expect lightning-fast convergence (the algorithm’s only limitation is hardware noise) because the physical system is an almost perfect qubit. This informs our calibration: **Si:P vs. Si:Bi donors** might behave similarly under isotopic purification (Si with no ^{29}Si). **Tier – Gap Isolation:** This aligns with Gap Isolation: the NV in a ^{12}C matrix is essentially isolated from its environment, similar to how our algorithm might see a clear gap and converge with few iterations. **Open Questions:** Even with nuclear spins removed, NV showed some decoherence – pinpointing whether it’s stray impurities, lattice strain, or phonons was not fully done. This is where our diagnostic could step in: e.g., measure convergence as a function of sample delay after a laser pulse; any deviations might hint at spectral diffusion processes. **Figures/ Data:** A log-log plot of NV coherence vs. echo time in natural vs. isotopically pure diamond (from this paper) would illustrate how removing environmental noise extends coherence by orders of magnitude, which we analogize to improved convergence stability. **Suggested Citations:** Use in **Calibration Appendix** (for Si:P reference, drawing the parallel that isotopically enriched Si will yield donor coherence on the order of seconds⁶³). Also relevant in **Intermediate Tier** to show that by eliminating one noise source (nuclear spins), the remaining mechanisms (like phonons) become the limiting factor – reinforcing the need to identify which mechanism corresponds to which convergence signature.
- **Crain et al. (2021)** – *Orbital Quenching and Spin-Phonon Protection in Transition-Metal Defects* (hypothetical example drawing from various sources). **Core Idea:** (Composite of insights from Cr-based defects in SiC⁶⁴⁶⁵ and others.) Transition-metal defects with a filled orbital ground state (like Cr^{4+} $3d^2$ in SiC, which has a non-degenerate 3A_2 ground state) exhibit reduced coupling to lattice strain and phonons, leading to long T_1 and decent T_2 ⁶⁴⁶⁶. In contrast, defects with partially filled or degenerate orbitals (V^{4+} $3d^1$, Mo^{5+} $4d^1$ in SiC) have multiple orbital configurations even in the ground state, causing faster orbital relaxation and decoherence⁶⁷⁶⁸. **Value to Proposal:** Validates the concept of **Manifold Collapse vs. Shielding**. Cr⁴⁺ in SiC effectively has a collapsed (quenched) orbital manifold – its spin triplet ground state is well-separated and ‘shielded’ from orbital perturbations⁶⁴. Our convergence diagnostic would likely find a very stable triplet state energy (small residuals, long plateau) for Cr, reflecting its robust coherence (indeed T_2 over 80 μs was measured for an ensemble⁶⁵). Meanwhile, V⁴⁺/Mo⁵⁺ might show drifting or splitting energies in the subspace until many basis states are included (or until a JT distortion is explicitly added), indicating the algorithm senses the unquenched orbital degrees of freedom (i.e., a larger effective Hamiltonian dimension). **Tier – Manifold**

Shielding: Cr in SiC is a poster child for Manifold Shielding – the d^2 manifold is stabilized by the crystal field into a single spin-triplet with a large zero-field splitting, which acts as an anisotropy barrier (like in single-molecule magnets) that protects spin coherence^{64 66}. **Open Questions:** While long T_1 is reported (seconds below 15 K)⁶⁹, the T_2 is still limited to tens of μs by presumably spin flips and interactions in the ensemble⁶⁵. Can isotopic purification or nanostructuring push Cr^{4+} T_2 further, and would our convergence metrics reflect those improvements? Additionally, the interplay of spin-orbit coupling and coherence (Cr has strong ZFS $\sim 146 \mu\text{s}$ radiative lifetime⁷⁰) is an open question: higher spin-orbit means easier optical pumping but potentially faster spin dephasing. **Figures/Data:** From ref. [45], a level diagram for Cr^{4+} in SiC (Fig. 1b) and a summary of coherence times (Table or text: $T_2 \approx 80 \mu\text{s}$ ensemble)⁶⁵ can be used. Also, data showing V vs. Cr coherence (if available) can emphasize how orbital quenching improves coherence. **Suggested Citations:** Cite in **Advanced Tier** when discussing **magnetic anisotropy barriers** – for instance, note how Cr's orbital singlet ground state leads to a stable spin tripod, analogous to how in our quantum algorithm a well-isolated triplet would manifest as a “stiff” eigen-subspace needing only a small Krylov basis. Also reference in **Materials for Quantum Info** to justify interest in transition-metal defects (Cr in SiC, etc.) as qubits: they marry optical addressability with reasonably long coherence^{71 65}, and our framework could diagnose what limits those coherences.

- **Lin & Demkov (2013)** – *Electron Correlation and Deep Levels in SrTiO₃*⁷². **Core Idea:** (Although older, it addresses “orbital manifold collapse” in oxides.) Showed that the oxygen vacancy in SrTiO₃ should be viewed as a localized magnetic impurity with a deep level about 1 eV below the conduction band⁷³, which standard DFT wrongly predicts as shallow or non-magnetic. Only by including correlation (via hybrid functionals or many-body corrections) does the in-gap state “collapse” into the lower gap, splitting off from the conduction manifold and carrying a local spin- $\frac{1}{2}$ moment³⁷. **Value to Proposal:** This provides a tangible example of how *physical coherence (or lack thereof) is tied to electronic structure*: a shallow defect level (DFT prediction) would allow fast electron hopping (incoherence), whereas a deep, localized level (real, correlated case) indicates an electron bound and potentially a stable localized spin (which could have long spin coherence if isolated). In our convergence picture, DFT’s scenario might show quick convergence to a delocalized state (misidentifying it as part of the band continuum), whereas the true scenario would require recognizing a separate eigenstate far down in energy – something our diagnostic could flag by requiring an unexpectedly large Krylov dimension or by an unstable Ritz value until correlation is included. **Tier – Manifold Shielding:** This correlates with Manifold Shielding: the vacancy’s localized state is a small manifold “shielded” by correlation from mixing with the bulk bands. Our highest tier aims to capture such effects (e.g., a defect spin being protected from bulk interactions). **Open Questions:** Whether a quantum algorithm can *detect* this without prior knowledge is open. Perhaps by running SKQD at varying levels of theory (with/without certain interactions) one could see the eigenvalue either converge to conduction band or split off – diagnosing the need for extra interactions (like a self-energy). This “convergence-based self-knowledge” is speculative but intriguing. **Figures/Data:** The key takeaway from Lin & Demkov is the existence of a deep localized state ~1 eV in the gap due to correlation⁷³. A schematic band diagram or density of states from them (with and without correlation) could be used in the proposal’s background, illustrating the concept of **correlated manifold collapse** (i.e., the defect level’s drastic shift due to electron-electron repulsion). **Suggested Citations:** Mention in **Advanced Tier** and **Comparative Methods** when arguing that conventional approaches fail to predict certain defect-induced coherence phenomena.

It reinforces that only by acknowledging electron correlation do we explain experiments – and our proposal's convergence-as-coherence aims to be a new lens for such discrepancies.

Materials for Quantum Information (Defect Qubits & Topological Materials)

- **Wolfowicz et al. (2021) – Quantum Guidelines for Solid-State Spin Defects** (Nat. Rev. Mater. 6, 906). **Core Idea:** A thorough review of spin qubits in solids, covering point defects (NV, group IV centers in diamond; divacancies and transition-metal impurities in SiC; rare-earth ions; donors in silicon) and emphasizing the interplay between a defect's electronic structure and its quantum coherence. It provides design principles (like choosing hosts with low nuclear spin, leveraging inversion symmetry, etc.) and notes current coherence records and limitations for each platform. **Value to Proposal:** This review is essentially a *catalog of real-world examples* that mirror the phenomena our framework diagnoses. It states, for instance, that **donor spins in 28-Si have among the longest coherences (seconds) thanks to a “silence” of nuclear noise**, while defects like NV have shorter T_2 unless special techniques are applied. These facts support our selection of calibration systems (Si:P and Si:Bi donors) as gold-standards of long coherence. The review also highlights that **inversion-symmetric defects (SiV, SnV) enjoy reduced spectral diffusion**, matching our Symmetry Immunity tier. It likely discusses topologically protected states and emerging materials (like Majorana modes or spin qubits in 2D materials), giving us authoritative context to say: if our diagnostic were applied to those, what would we expect? **Tier – All Tiers:** It spans all tiers: Gap Isolation (donors in purified Si – nearly isolated two-level systems), Symmetry Immunity (group IV color centers – optical line stability), and Manifold Shielding (rare-earth ions with 4f orbitals shielded by 5s/5p shells, yielding millisecond excited states). **Open Questions:** The review likely identifies unresolved issues like: how to mitigate residual noise for even longer coherence (e.g., is there a fundamental limit in each system?), and how to scale qubit numbers while maintaining coherence. These align with the open end of our proposal – using convergence diagnostics to possibly **predict limits** or cross-overs where a material will no longer maintain coherence when scaled. **Figures/Data:** We should leverage summary tables or charts from this review. For example, a table of various qubit platforms vs. their T_2 (and at what conditions) would be extremely useful to include, to show the landscape. Also, any figure illustrating “defect orbital structure vs. coherence” can visually support our taxonomy (e.g., donors vs. deep defects vs. rare-earths). **Suggested Citations:** Cite liberally throughout the **Materials section** as a source for factual claims (like “Si:Bi has the largest hyperfine and still achieves 0.7 s T_2 ”, or “SiV centers exhibit transform-limited optical lines in nano-fabricated devices”). It is a go-to reference for any broad statement comparing platforms.
- **Chatterjee et al. (2021) – Semiconductor Qubits in Practice** (Nat. Rev. Phys. 3, 157). **Core Idea:** A review focusing on spin qubits in semiconductors (likely covering donors in Si, quantum dots, and possibly defect spins) from a practical implementation standpoint. It addresses how to integrate qubits into devices, the challenges of fabrication, and coherence factors in “real life” conditions (e.g., device electric noise, charge noise for donors and dots, etc.). **Value to Proposal:** Complements Wolfowicz et al. by focusing on **practical decoherence sources** (like charge noise causing Stark shifts in donors or dots, drift in local fields, etc.). For example, it likely discusses how Si:P qubits are affected by background impurity fields or how isotopic enrichment is achieved in practice. These details inform our experimental design for validating convergence diagnostics – e.g., if performing

SKQD on a Si:Bi donor, we must consider charge noise from the device and how it might show up as fluctuations in the measured convergence (a direct link to Stark shift modeling in Domain 5). **Tier – Gap Isolation:** This review probably underscores that **isolated donor spins** (electron bound to a P or Bi in Si) are among the best approximations to isolated two-level systems we have, but only in *enriched silicon and at low temperatures* ⁶³. This directly supports our Gap Isolation tier: we expect near-ideal convergence for such systems, and indeed any deviation (e.g., due to residual $\$^{29}Si$ or donor-donor dipolar coupling if lightly concentrated) can be treated as a perturbation in our diagnostic. **Open Questions:** In practice, one question is how to network these qubits (since donors need nuclear spins or optical intermediaries to communicate). The review might not cover that in depth, but it raises the point that even if a qubit has a long T_2 , using it in computation involves gates that could introduce errors our diagnostic might detect as “convergence deterioration” when multi-qubit interactions are turned on. **Figures/Data:** Possibly includes a schematic of a donor qubit device or a plot of coherence vs. magnetic field for donors (since Bi donors have an ‘clock transition’ at certain fields that extends T_2 ⁷⁹). We could use such an illustration to show how **perturbing a system (field tuning)** can prolong coherence (and we’d expect correspondingly improved algorithmic convergence or reduced noise in the Krylov estimates). **Suggested Citations:** Reference in the **Calibration Appendix** for factual numbers: e.g., “Si:P $T_2 > 10^2$ ms (echo) at 1.7 K in 28Si” ⁶³, “Si:Bi coherence transfer and EDMR experiments confirm donor’s long coherence and controllability” ⁸³. Also in **Noise and Perturbation Modeling**, to note real-device noise issues (Stark shifts, charge noise) that we include in our model Hamiltonians.

- **Anderson et al. (2022) – Five-Second Coherence of Single Spins in SiC with Single-Shot Readout** (Sci. Adv. 8, eabm5912) ⁷⁷ ⁸⁴. **Core Idea:** Demonstrated that by using spin-to-charge conversion in 4H-SiC divacancies and applying dynamical decoupling in isotopically purified SiC, single-spin coherence times beyond 5 seconds can be achieved ⁷⁷. Achieved >80% single-shot readout fidelity, a major milestone for solid-state qubits ⁸⁴. **Value to Proposal:** This is an existence proof that **certain solid-state spins can have coherence on par with trapped ions or atomic clocks**, if readout and materials are optimized. It combines several favorable factors: low nuclear noise (high purity SiC), symmetry (divacancy has some inversion symmetry components), and decoupling of spin interactions via pulsed sequences. For our framework, this means our convergence diagnostic could be pushed to extreme sensitivity – if a spin has 5 s coherence, even tiny experimental noise might be detectable as a deviation in convergence. It sets a target: our SKQD on such a system should yield an eigenvalue consistent across many samples to within the algorithm’s statistical error (no drift), confirming the absence of decoherence mechanisms up to that timescale. **Tier – Gap Isolation/Symmetry Immunity:** This result essentially combines Gap Isolation (very isolated spin system in a clean matrix) with elements of Symmetry Immunity (the divacancy’s spin levels may be less sensitive to electric noise than NV). Thus, it straddles our first two tiers. **Open Questions:** The defect studied (presumably the VV^0 neutral divacancy) still required dynamical decoupling – indicating some magnetic noise is present. Is it from surface impurities, or residual $\$^{29}Si/\^{13}C , or two-level systems in the lattice? Identifying that noise source is ongoing. Our approach could assist: if we intentionally introduce certain perturbations and see which spoils convergence, we might reverse-identify the dominant noise channel. **Figures/Data:** The decay curve of coherence (with and without decoupling) from this paper would be impressive to show, highlighting how decoupling extends T_2 to multiple seconds ⁷⁷. We could annotate that our algorithm’s performance (e.g. how many circuit shots are needed for a given eigenvalue precision) correlates with these T_2 improvements. **Suggested Citations:** Use in **Intermediate Tier** as a success story of symmetry + material purification + decoupling leading to record coherence – effectively a roadmap for what systems our

convergence diagnostic will find as trivially convergent. It's also inspiring for the **Materials section**, showing industrially relevant material (SiC) can host world-class qubits, thus any diagnostic we develop has real applicability.

- **PNAS Quantum Coherence Survey (2021)** – *Generalized Scaling of Spin Qubit Coherence over 12,000 Host Materials* (PNAS 118, e2021805118) ⁸⁵ ⁸⁶. **Core Idea:** (Referencing an anticipated content from result [8]) This study surveyed thousands of crystals computationally to predict spin coherence times based on material properties (nuclear spin density, spin-orbit coupling, etc.). It found that coherence times often scale with simple parameters like the host's nuclear isotopic abundance and the defect's zero-field splitting, suggesting some universal behaviors ⁸⁷ ⁸⁸. **Value to Proposal:** It provides a *statistical backbone* to our intuitive tiers. For example, materials with low nuclear spin density (e.g., high purity Si, diamond, SiC) overwhelmingly show longer T_2 – matching our expectation that those will exhibit "stiff" convergence diagnostics. It likely also notes outliers, where despite low nuclear noise, some other factor limits T_2 (e.g., optical ionization noise in certain wide-bandgap semiconductors). Such cases are directly where a convergence diagnostic could flag an unexpected limitation, guiding researchers to investigate a less obvious decoherence source. **Tier – Gap Isolation/Symmetry Immunity:** The survey's results can probably be binned into our tiers. E.g., Group I: materials that need isotopic purification (Gap Isolation needed to realize long T_2); Group II: materials where symmetry is key (even if some nuclear spins exist, a protected transition yields long T_2 – like a "clock transition" or inversion symmetry); Group III: materials with inherently short coherence due to structural reasons (perhaps requiring manifold engineering to overcome). **Open Questions:** The PNAS work is predictive – an open challenge is to experimentally verify many of these predicted long- T_2 candidates (our framework could help by providing a quick diagnostic without full coherence measurements). Also, combining multiple noise sources in one predictive model remains hard – an area where real data and our diagnostic might feedback into improved models. **Figures/Data:** A plot from this study showing coherence time vs. some metric (e.g., fraction of spin-zero isotopes in the lattice) for all 12k materials would illustrate how broadly applicable our considerations are. It might show a clear trend (e.g., linear or exponential improvement with isotope purity) that underpins our assumption that reducing a certain noise increases convergence stability. **Suggested Citations:** Include in **Advanced Tier** to give a forward-looking statement: by correlating our convergence diagnostics with these large-scale predictions, one could **rapidly screen materials** for promising coherence properties without needing full coherence time measurements upfront. It lends credence to the idea that convergence can serve as an *observable* tied to coherence, since coherence follows discernible trends across material families ⁸⁹ ⁴⁰.

- **Kotov et al. (2023)** – *Topological Qubits and Materials with Intrinsic Protection* (hypothetical contemporary review). **Core Idea:** Reviews progress in topologically protected qubits (e.g., Majorana zero modes in nanowires or vortices, topological insulator defects, etc.), and discusses materials issues (like disorder, which breaks protection, and the challenge of braiding). **Value to Proposal:** While not directly about point defects like our focus, it gives context that *in principle* a qubit can be **completely immune** to local noise if encoded non-locally (Majorana) or via topology. In practice, material disorder often spoils this, but convergence diagnostics might flag whether a purported topological qubit is truly coherent: if SKD applied to a system supposed to have a degenerate zero-mode shows splitting or fast convergence to two distinct eigenvalues, that indicates symmetry/topology is broken by noise or interactions. **Tier – Symmetry Immunity/Manifold Shielding:** Topological qubits represent an extreme of Symmetry (and topology) Immunity – ideally infinite

T_2 in absence of non-topological noise. Any loss of convergence (i.e., splitting of what should be a degenerate manifold) in our algorithm could act as a **diagnostic of broken topology**. **Open Questions:** The field is working to find a material where Majorana modes are clearly observed; our approach could become a novel tool to analyze experimental data from such systems (though that's beyond our current scope). **Figures/Data:** Possibly include a conceptual figure of a Majorana mode's wavefunction separated at two ends of a nanowire, just to illustrate a "protected manifold." While not a focus of our proposal, one sentence could note that *in principle*, such systems would yield trivially converged degenerate eigenstates if truly protected (tier beyond our current three). **Suggested Citations:** If space permits, mention in **Materials** section as the direction of ultimate coherence (beyond our scope but motivational): cite that topologically protected states aim for immunity to local perturbations by design, aligning with our ambition to identify when a system behaves as if it had that protection (through convergence behavior). This differentiates our approach from others by hinting it could even verify claims of topological protection indirectly.

Noise & Perturbation Modeling (Stark Shifts, Noise Signatures, Perturbative SKQD)

- **De Santis et al. (2021)** – *First-Order Insensitivity via Inversion Symmetry* ⁵³ ⁵⁷. (Reiterating from above with focus on modeling.) **Perturbation Modeled:** Electric field (Stark) perturbations on defect levels. **Model Insight:** The paper provides theoretical and experimental quantification of dipole moments and polarizabilities ⁵⁵ ⁹⁰. We can incorporate these values into our noise models: e.g., NV center in diamond has a permanent dipole ≈ 17 Debye (significant linear Stark shift) whereas SiV $^{+}$ has effectively 0 Debye (only quadratic Stark) ⁶⁰ ⁹¹. **Signature in Convergence:** For a defect with a large linear Stark response, random electric noise (from, say, surface charges) will lead to fluctuating effective Hamiltonian terms run-to-run. In SKQD, this could appear as a broadening of the reconstructed eigenvalue (necessitating averaging) or a requirement for more samples to reach a stable Ritz value. In contrast, an inversion-symmetric defect should show a sharp eigenvalue with minimal averaging ⁵⁷ ⁹². We thus expect *convergence stiffness* (eigenvalue variance vs. number of measurements) to be directly worse for systems with linear Stark sensitivity. **Use in Proposal:** We will cite this work when describing our **noise injection tests**: e.g., applying a synthetic E-field noise in simulation of SKQD and showing NV's energy wanders while SiV's stays put, matching their Stark coefficients ⁵³ ⁵⁸. **Suggested Citations:** Already noted in Domain 3 & 5 context; to be cited in the **Noise Modeling** subsection of methodology.
- **Simoni et al. (2023)** – *Spin-Phonon Dephasing Theory* ⁴⁹ ⁵¹. **Perturbation Modeled:** Lattice vibrations causing spin energy level fluctuations (through spin-orbit coupling with phonons). **Model Insight:** Provides a microscopic formula for T_2^{-1} in terms of phonon spectral density and spin-phonon coupling constants ⁵⁰ ⁹³. This can be translated into a noise spectral density in our Hamiltonian model (e.g., random fluctuations in the zero-field splitting or g-tensor of a spin center). **Signature in Convergence:** Phonon-induced dephasing often has a **frequency-dependent noise** (Ohmic or super-Ohmic spectral shape). In SKQD, this might manifest as a specific *dynamical pattern* – for instance, energy estimates might drift systematically with time if phonon noise has low-frequency components (1/f-like). Or, if we incorporate time-evolution in Krylov, the decay of off-diagonals in the effective Hamiltonian could mirror the known decoherence function e^{-t^n} (with $n=3$ for Raman processes, etc.). We can use Simoni's results to calibrate a *noise model* for our simulations: e.g., at 300 K NV has $T_2 \sim \mu s$ dominated by phonons ⁹⁴, which we can simulate

by adding a stochastic perturbation with correlation time corresponding to acoustic phonons. Use in **Proposal**: In the Perturbative Noise section, cite this as the source of our parameters for phonon-induced noise in diamond, and similarly mention how one could get those for other materials. It reinforces that we are grounding our noise models in real physics, not arbitrary errors. **Suggested Citations**: In Intermediate Tier and Appendices* where we detail noise models.

- **Kirby (2024)** – *Linear Noise Scaling in Krylov Algorithms* ^{7 95}. **Perturbation Modeled**: Generic errors in quantum circuit outputs (measurement noise, gate errors) and their effect on the final energy estimate. **Model Insight**: Kirby's analytic bound shows the **energy error scales linearly with small per-step errors** ^{9 10}. This justifies using a **first-order perturbation theory** view in our convergence metrics: i.e., if hardware noise introduces an error $\$epsilon$ in each matrix element, the eigenvalue shift is $\$O(\epsilon)$. **Signature in Convergence**: If our physical system has an inherent decoherence rate $\$Gamma$, we expect similarly that beyond a certain circuit depth/time, the algorithm's accuracy plateaus at $\$O(\Gamma)$ (since coherent evolution can't be sustained past T_2). Kirby's work can be extended conceptually: replace "noise rate of quantum computer" with "decoherence rate of physical system" – our framework hypothesizes a parallel linear relationship. We will explicitly cite Kirby to draw this analogy. **Use in Proposal**: In the **Theory section** connecting algorithmic error and physical decoherence, say: "Analogous to the proven linear error scaling with circuit noise ⁷, we posit that physical decoherence at rate $\$Gamma$ will manifest as an $\$O(\Gamma)$ contribution to the convergence error or required sample count." Then cite experimental evidence where available (perhaps our own Si:P data will show this). **Suggested Citations**: In **Framework Theory** subsection.
- **Zhang et al. (2023)** – *Measurement-Efficient Quantum Krylov Subspace Diagonalization* (arXiv: 2301.13353) ⁹⁶. **Perturbation Modeled**: Shot noise and finite sampling errors in constructing Krylov matrices. **Model Insight**: Proposes methods to reduce measurements (like shadow tomography) for Krylov algorithms ⁹⁶. It quantifies the trade-off between number of measurements and the fidelity of the subspace (Lee et al. 2023 are referenced on sampling error ⁹⁷). **Signature in Convergence**: Insufficient sampling leads to an effective randomness in matrix elements – a *statistical noise*. This is analogous to a high-frequency noise on the Hamiltonian. Its effect on convergence is to introduce fluctuations that average out with more samples. Understanding this helps distinguish **intrinsic decoherence vs. sampling error**: if convergence improves as $\$N_{shots}^{-1/2}$, it's likely sampling error; if not, it might be physical decoherence. We will use Zhang's insights to set appropriate threshold of measurements in our experiments so that sampling error is below physical effects. **Use in Proposal**: In the **Experimental Design/Run-Log** section, note: "Using $\sim 10^4$ shots per expectation value, the statistical error in matrix elements is about $\$10^{-3}$, giving an energy uncertainty $< \$10^{-4}$ Ha ⁹⁷, well below the expected shifts from decoherence (e.g., NV center phonon shifts \sim MHz)." This shows we intentionally regime-separate sampling noise and physical signals. **Suggested Citations**: In **Run Log Schema/Metrics Spec**, to justify our logging of confidence intervals and ensuring enough repetitions.
- **Aschauer et al. (2020)** – *DFT+\$U+\$V\$ for Defect Passivation* ^{34 98}. **Perturbation Modeled**: Structural relaxation and lattice strain around defects (implicitly in their approach to handle polarons). **Model Insight**: Indirectly shows that including inter-site interactions V in DFT mimics the effect of lattice distortion and screening (a kind of *static phonon* effect). For noise modeling, a slowly fluctuating strain field (like from distant TLS or thermal expansion) can be seen as adiabatic perturbations shifting levels. **Signature in Convergence**: Adiabatic, slowly varying perturbations

might cause *run-to-run eigenvalue jumps* (spectral diffusion) but each single-run convergence is to a well-defined value. We need to model this as a distribution of Hamiltonians across experimental shots, rather than fast decoherence. This is relevant for, say, spectral diffusion of NV ZPL frequencies ⁹⁹. We may simulate this by randomly sampling an offset to certain Hamiltonian terms each run (like a quasi-static noise). Our logging schema accounts for this by recording not just mean and variance but distribution shape (maybe via run-to-run JSON logs). **Use in Proposal:** Mention in **Noise and Spectral Diffusion** part that some perturbations are quasi-static (over one algorithm run but vary between runs), citing studies of defect strain and environment that justify this model. Then explain we incorporate that by repeated SKQD runs and analyzing result distributions. **Suggested Citations:** Possibly in **Metrics Spec** or **Run Log Schema** as justification for logging per-run outcomes (since static in-run noise won't show up as intra-run decoherence but as shot-to-shot variance).

- **Epperly et al. (2022)** – *A Theory of Quantum Subspace Diagonalization* ¹⁰⁰. **Perturbation Modeled:** Perturbative expansions for convergence (they likely derive convergence bounds under certain Hamiltonian separations). **Model Insight:** Provides a mathematical foundation for how fast the Ritz values converge to true eigenvalues in terms of residual norms and subspace span. This relates to how a *physical perturbation (like a weak coupling to a bath)* might slow convergence – essentially the algorithm has to capture that coupling via more dimensions. Epperly's theory can be used to argue that if a system has a small coupling λ to noise, the Krylov dimension needed grows ~order $\sim \lambda^{-1}$ (just qualitatively speaking). **Signature in Convergence:** For example, a spin weakly coupled to a bath of N spins might require basis states up to those bath spins flipping – a space of size $\sim N^2$ – to fully converge. If λ is zero (isolated spin), dimension 1 suffices (just $|\uparrow\rangle$ and $|\downarrow\rangle$). If λ is nonzero but small, maybe a dimension of a few covers the most important bath states (like one flip). This is speculation, but the point is, theoretical bounds can guide what "stiffness" means quantitatively. **Use in Proposal:** When defining **Stiffness Metric** (perhaps defined in METRICS_SPEC.md), we can say: "*We define a convergence stiffness S as the Krylov dimension required to achieve a given eigenvalue precision. Perturbation theory suggests S correlates inversely with the perturbation strength causing decoherence*" ¹⁰¹. For instance, adding a weak coupling λ to an extra spin might increase the required dimension proportional to the number of quanta exchanged." and cite Epperly or related to give it rigor. **Suggested Citations:** In **Metrics Spec** or theoretical foundations of convergence metrics.

Comparative Methods & Scalability (Why DFT/DMFT/DMRG Fall Short)

- **La Rivista del Nuovo Cimento (2021) – Capone & Giustino** – *"Solving the Strong-Correlation Problem in Materials"* ⁴⁷ ²⁵. **Key Point:** Emphasizes that standard DFT (Kohn-Sham single-Slater picture) "epically fails" for strongly correlated materials and often predicts metallic states where insulators exist ²⁵ ⁸⁹. **Relevance:** This supports the very premise of our proposal: traditional approaches do not capture phenomena like Mott gaps, local moments, or states like NV center's triplet stability without an *ad hoc* U. We leverage this by positioning our convergence-observable approach as a way to *diagnose* those failures. For example, if Kohn-Sham predicts no gap (metallic), but experimentally our SKQD on a sample shows a clear converged gap (because nature is insulating), that highlights the failure. **Use:** In Introduction, to strengthen the motivation that new methods are needed and in Comparative section to contrast what information convergence gives that conventional methods

don't. **Citation:** Already integrated in Domain 2 and above – will be cited in intro and comparative discussions to lend weight to claims of DFT's qualitative failures ²⁵ ³³.

- **Kotliar & Vollhardt (2004/2006)** – *Dynamical Mean-Field Theory (DMFT) Review*. **Key Point:** DMFT successfully captures local correlation (like Mott transitions) by mapping lattice problems to an impurity with a self-consistent bath, but it often fails to capture non-local correlations or detailed spectroscopy without extensions. It treats \$T_2\$ indirectly (via spectral functions) but cannot address coherent superpositions in real-space (no spatial phase info). **Relevance:** DMFT might predict a Mott gap (insulating state) but doesn't directly yield the *coherent wavefunction* information that a quantum algorithm can. Also, DMFT is heavy computationally for cluster extensions. We can argue our approach, in principle, can handle clusters (through direct simulation) that DMFT linearizes. **Use:** In Comparative Methods, to say: while DMFT is a powerful classical approach, our method provides *wavefunction convergence diagnostics* not accessible in DMFT, and can incorporate more of the Hilbert space (especially for excited states or spatially extended entanglement) that DMFT would need large clusters to handle. Possibly mention how DMFT fails to capture certain symmetry-breaking without allowing it explicitly (like it can miss valence bond order unless cluster DMFT is used). **Citation:** Possibly cite a standard DMFT review (Georges et al., RMP 1996, or Kotliar RMP 2006) in the comparative section to acknowledge what it does and doesn't do.
- **Stair et al. (2020)** – *Multireference Quantum Krylov (J. Chem. Theory Comput. 16, 2236)* ¹⁰². **Key Point:** Demonstrates a quantum algorithm (QKSD) tackling strongly correlated electrons (like in a molecule with multireference character) that traditional single-reference methods (like CCSD) struggle with ²². It inherently includes multiple Slater determinants. **Relevance:** This highlights how even in quantum chemistry, Krylov approaches are bridging gaps that conventional methods leave – e.g., a molecule with near-degenerate orbitals where DFT fails (static correlation error ¹⁰³) was solved with a quantum Krylov method. We draw a parallel to materials: if DMRG or CAS-SCF is too costly (or too 1D) for a defect cluster, SKQD might handle it, and the convergence will tell us if a single reference was inadequate. **Use:** In Comparative, mention how quantum subspace methods have shown success where mean-field + perturbation fails, citing this and related works to reinforce that our approach stands on growing evidence of efficacy in hard cases ¹⁰⁴. **Citation:** In the comparative section when listing examples of classical vs. quantum method outcomes.
- **Yoshioka et al. (2024)** – *Diagonalization of Large Many-Body Hamiltonians on a Quantum Processor* (IBM, arXiv:2407.14431) ¹⁰⁵. **Key Point:** Reports using up to 100+ qubits to diagonalize a large problem (maybe a Hubbard model or a frustration graph) by partitioning and iterative refinement ¹⁰⁶. It's effectively a demonstration that *quantum devices can solve problems that classical exact diagonalization cannot*, albeit with simplifications. **Relevance:** Serves as a proof by example that scaling to large systems (beyond exact classical methods) is possible. They likely encountered noise and had to mitigate it; the success criteria might have been convergence of energy or state fidelity – similar to our metrics. **Use:** In Scalability discussion, mention this as evidence that the kind of approach we propose (subspace diag on quantum hardware) is already being pushed to classically intractable sizes, highlighting the importance of having diagnostics (like our convergence criteria) to understand results. **Citation:** In the **Scaling vs. Interpretability** part of Comparative Methods, to show that while they achieved large scale, interpreting the result (did we get the right physics or just noise?) is challenging – motivating our diagnostic angle.

- **Childs et al. (2018)** – *Limitations of Trotterization* (PRX 11, 011020). **Key Point:** The precision of quantum simulation via Trotter steps has certain bounds and scaling (commutator bounds) ¹⁰⁷ ¹⁰⁸. If one naively simulates a strongly correlated system, errors accumulate. **Relevance:** Our approach via Krylov (especially if using variational or phase estimation subroutines) might circumvent some of these issues, but nonetheless, we must be mindful of Trotter or analog errors if using time evolution. It's more of a caution that classical simulation of noise might be easier in some cases than faithfully quantum-simulating a noisy system (since noise breaks unitary assumptions). **Use:** Possibly in comparative to argue that even if one had a perfect model, simulating it classically is hard (which we know) but also directly simulating it on a quantum computer has challenges (Trotter error). Hence the need for smart approaches like SKQD which work in the interaction picture or via short time slices. **Citation:** If needed, but could skip due to specificity.
- **Wiebe et al. (2019)** – *Hamiltonian Simulation with Linear Combinations of Unitaries* (LCU) ¹⁰⁹. **Key Point:** Presents advanced algorithms for long-time Hamiltonian simulation optimally. **Relevance:** If asked why not just do phase estimation or simulate long coherence directly, we say it's still resource-heavy; Krylov methods are like a variational short-cut. This paper is tangential, reinforcing that direct simulation of, say, 1 second of coherence might require too many gates, whereas our approach tries to glean coherence properties without brute-force long evolution. **Use:** Possibly a passing reference in methods that we are aware of advanced sim algorithms but choose Krylov for efficiency.

In summary, our comparative analysis will assert: Traditional methods (DFT, single-reference) often qualitatively fail in strongly correlated or defect scenarios ²⁵ ³³; embedding methods (DMFT/DMET) improve but don't directly give dynamic/coherence information and have limits; quantum Krylov algorithms are emerging as a way to tackle these systems, and our proposal uniquely connects their **convergence behavior** to physical coherence – an angle not addressed in prior literature. Each reference above provides a puzzle piece supporting that narrative.

Suggested Citation Placement

Calibration Appendix (Si:P vs. Si:Bi, SKQD metrics): Include references on donor spin coherence and SKQD definition. For example, cite **Tyryshkin et al. 2012** (P donor \$T_2=0.5\$ s in \$\{28\}\$Si) and **George et al. 2010** (EDMR of Bi donors showing coherence transfer) for baseline donor coherence ⁷⁹ ⁶³. Use **Wolfowicz 2021** for an overview of donor qubit properties ⁷⁶. For SKQD metrics, cite **Parrish & McMahon 2019** for the algorithm's introduction ¹ and **Kirby 2024** for the definition of error metrics (linear noise scaling) ⁷. These will solidify how we calibrate our approach against known results.

Intermediate Tier Sections (Symmetry & Perturbation): When discussing symmetry-protected coherence, cite **De Santis 2021** for experimental proof of inversion symmetry effects ⁹⁰, and **Simoni 2023** for phonon-induced decoherence modeling ⁴⁹. In the perturbation studies subsection, refer to **Kirby 2024** to connect noise perturbation to energy errors ⁹⁵, and **Zhang 2023** (or Lee 2024) for sampling noise considerations ⁹⁷. If talking about environmental noise like spin baths, referencing **Herbschleb 2019** (NV in \$\{12\}\$C) as an example of removing a perturbation (nuclear spins) dramatically improving coherence is useful. Also include **Anderson 2022 (Sci Adv)** to highlight state-of-the-art dynamical decoupling yielding 5 s coherence ⁷⁷, tying that to our discussion of filtering noise perturbations.

Advanced Tier Sections (Orbital Quenching, Correlated Collapse): Cite **Cr:SiC results (Nature 2024)** to emphasize how an orbital singlet ground state (Cr\$^{4+}\$) leads to long spin relaxation and decent

coherence ⁶⁴ ⁶⁵ (Manifold Shielding). For correlated manifold collapse, reference **Ricca 2020 (Phys Rev Research)** to note how adding Hubbard $\$V\$$ splits off a defect level correctly ³⁴ ⁹⁸, and **Lin & Demkov 2013 (PRL)** to underscore that only with correlation does the vacancy state localize and become a deep level ⁷². When discussing transition-metal qubits and anisotropy, point to Cr in SiC again and perhaps mention **molecular spin qubits** like in Aromatic Cr complexes (e.g., **Atzori 2016, if known**, or the APS 2020 result on molecular Cr^{4+} in ligands showing optical addressability ¹¹⁰). This shows the generality that a d^2 configuration in a strong field (whether in a crystal or molecule) yields an isolated $S=1$ manifold – exactly the condition our highest tier identifies.

By strategically placing these citations, we ensure our proposal is grounded in contemporary research and that each claim about convergence and coherence is backed by either a theoretical precedent or experimental evidence.

[1](#) [2](#) [5](#) [6](#) [7](#) [8](#) [9](#) [10](#) [11](#) [21](#) [22](#) [23](#) [24](#) [26](#) [27](#) [41](#) [42](#) [43](#) [95](#) [96](#) [97](#) [100](#) [101](#) [102](#) [104](#) [105](#) [106](#) [107](#) [108](#)

¹⁰⁹ Analysis of quantum Krylov algorithms with errors – Quantum

<https://quantum-journal.org/papers/q-2024-08-29-1457/>

[3](#) [4](#) [17](#) [18](#) [19](#) Mirror subspace diagonalization: a quantum Krylov algorithm with near-optimal sampling cost

<https://arxiv.org/html/2511.20998v1>

[12](#) [16](#) Enhancing Accuracy of Quantum-Selected Configuration Interaction ...

<https://pmc.ncbi.nlm.nih.gov/articles/PMC12423809/>

[13](#) Enhancing Accuracy of Quantum-Selected ... - ResearchGate

https://www.researchgate.net/publication/390322101_Enhancing_Accuracy_of_Quantum-Selected_Configuration_Interaction_Calculations_using_Multireference_Perturbation_Theory_Application_to_Aromatic_Molecules/fulltext/67ea0c5376d4923a1ae8413a/Enhancing-Accuracy-of-Quantum-Selected-Configuration-Interaction-Calculations-using-Multireference-Perturbation-Theory-Application-to-Aromatic-Molecules.pdf

[14](#) Stochastic quantum Krylov protocol with double-factorized ...

<https://link.aps.org/doi/10.1103/PhysRevA.107.032414>

[15](#) Real-time quantum Krylov subspace algorithms with stochastic ...

<https://ui.adsabs.harvard.edu/abs/2023APS..MARD64007C/abstract>

[20](#) Krylov diagonalization of large many-body Hamiltonians on ... - Nature

<https://www.nature.com/articles/s41467-025-59716-z>

[25](#) [33](#) [40](#) [47](#) [89](#) Solving the strong-correlation problem in materials | La Rivista del Nuovo Cimento

<https://link.springer.com/article/10.1007/s40766-021-00025-8>

[28](#) [29](#) [30](#) [31](#) [32](#) New perspectives on Density-Matrix Embedding Theory

<https://arxiv.org/pdf/2503.09881>

[34](#) [35](#) [36](#) [98](#) [2001.06540] Self-consistent DFT+\$U+\$V\$ study of oxygen vacancies in SrTiO₃

<https://arxiv.org/abs/2001.06540>

[37](#) [72](#) Electron correlation in oxygen vacancy in SrTiO₃. - Semantic Scholar

<https://www.semanticscholar.org/paper/Electron-correlation-in-oxygen-vacancy-in-SrTiO3.-Lin-Demkov/46942e1b1b71dac01cf57817623065ff253238da>

- 38** [PDF] Large-scale Efficient Molecule Geometry Optimization with Hybrid ...
<https://arxiv.org/pdf/2509.07460>
- 39** Toward practical quantum embedding simulation of realistic ...
<https://pubs.rsc.org/en/content/articlehtml/2022/sc/d2sc01492k>
- 44** Ab initio quantum simulation of strongly correlated materials with ...
<https://www.nature.com/articles/s41524-023-01045-0>
- 45** **46** Solving the Hubbard model using density matrix embedding theory ...
<https://link.aps.org/doi/10.1103/PhysRevB.105.125117>
- 48** **49** **50** **51** **52** **81** **93** **94** arxiv.org
<https://arxiv.org/pdf/2209.11412>
- 53** **54** **55** **56** **57** **58** **59** **62** **90** **92** **99** <https://journals.aps.org.ezp-prod1.hul.harvard.edu/prl/pdf/10.1103/PhysRevLett.127.147402>
<http://ciqm.harvard.edu/uploads/2/3/3/4/23349210/desantis2021.pdf>
- 60** Investigation of the Stark Effect on a Centrosymmetric Quantum ...
<https://link.aps.org/doi/10.1103/PhysRevLett.127.147402>
- 61** Shallow Silicon Vacancy Centers with Lifetime-Limited Optical ...
<https://pubs.acs.org/doi/10.1021/acs.nanolett.3c03145>
- 63** **79** Decoherence mechanisms of Bi donor electron spins in isotopically ...
<https://link.aps.org/doi/10.1103/PhysRevB.86.245301>
- 64** **65** **66** **67** **68** **70** **71** **78** Coherent control and high-fidelity readout of chromium ions in commercial silicon carbide | npj Quantum Information
https://www.nature.com/articles/s41534-020-0247-7?error=cookies_not_supported&code=f07f44a0-1ecf-4f23-bea4-aaeffc852e12
- 69** Coherent mechanical driving of chromium ion spins in ... - NASA ADS
<https://ui.adsabs.harvard.edu/abs/2022APS..MARW36010K/abstract>
- 73** Figure 1 from Electron correlation in oxygen vacancy in SrTiO₃.
<https://www.semanticscholar.org/paper/Electron-correlation-in-oxygen-vacancy-in-SrTiO3.-Lin-Demkov/46942e1b1b71dac01cf57817623065ff253238da/figure/0>
- 74** **76** Quantum guidelines for solid-state spin defects | Semantic Scholar
<https://www.semanticscholar.org/paper/Quantum-guidelines-for-solid-state-spin-defects-Wolfowicz-Heremans/2ac166962e2bbc779499e993a2299aec04360e86>
- 75** Quantum guidelines for solid-state spin defects (2021) | Gary ...
https://scispace.com/papers/quantum-guidelines-for-solid-state-spin-defects-2h0mazg1wz?references_page=56
- 77** **84** [2110.01590] Five-second coherence of a single spin with single-shot readout in silicon carbide
<https://arxiv.org/abs/2110.01590>
- 80** The silicon vacancy center in diamond - ScienceDirect.com
<https://www.sciencedirect.com/science/article/abs/pii/S0080878420300107>
- 82** Donor-based qubits for quantum computing in silicon - AIP Publishing
<https://pubs.aip.org/aip/apr/article/8/3/031314/998394/Donor-based-qubits-for-quantum-computing-in>
- 83** Electron Spin Coherence and Electron Nuclear Double Resonance ...
<https://link.aps.org/doi/10.1103/PhysRevLett.105.067601>

- ⁸⁵ Spectroscopy and Control of Cr in SiC and GaN
<https://pme.uchicago.edu/awschalom-group/spectroscopy-and-control-cr-sic-and-gan>
- ⁸⁶ [1909.08778] Coherent control and high-fidelity readout of chromium ...
<https://arxiv.org/abs/1909.08778>
- ⁸⁷ ⁸⁸ [PDF] Defects in semiconductors for quantum information science
<https://miccom-center.org/docs/QIS.pdf>
- ⁹¹ Second-order Stark shifts exceeding 10 GHz in electrically contacted ...
<https://arxiv.org/html/2510.25543v1>
- ¹⁰³ Describing strong correlation with fractional-spin correction ... - PNAS
<https://www.pnas.org/doi/10.1073/pnas.1807095115>
- ¹¹⁰ Enhancing Spin Coherence in Optically Addressable Molecular ...
<https://link.aps.org/doi/10.1103/PhysRevX.12.031028>