Quasi-degenerate extension of local *N*-electron valence state perturbation theory with pair-natural orbital method based on localized virtual molecular orbitals

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Chemical phenomena involving near-degenerate electronic states, such as conical intersections or avoided crossing, can be properly described using quasi-degenerate perturbation theory (QDPT). This study proposed a highly scalable quasi-degenerate second-order *N*-electron valence state perturbation theory (QD-NEVPT2) using the local pair-natural orbital (PNO) method. Our recent study showed an efficient implementation of the PNO-based state-specific (SS) NEVPT2 method using orthonormal localized virtual molecular orbitals (LVMOs) as an intermediate local basis. This study derived the state-coupling (or off-diagonal) terms to implement QD-NEVPT2 in an alternative manner to enhance efficiency based on the internally contracted basis (ICB) and PNO overlap matrices between different references. To facilitate further acceleration, a local resolution-of-the-identity (RI) three-index integral generation algorithm was developed using LMOs and LVMOs. Although the NEVPT2 theory is considered to be less susceptible to the intruder-state problem (ISP), this study revealed that it can easily suffer from ISP when calculating high-lying excited states. We ameliorated this instability using the imaginary level shift (LS) technique. The PNO-QD-NEVPT2 calculations were performed on small organic molecules for the 30 lowest-lying states, as well as photoisomerization involving the conical intersection of 1,1-dimethyldibenzo[b,f] silepin with a *cis*-stilbene skeleton. These calculations revealed that the PNO-QD-NEVPT2 method yielded negligible errors compared to the canonical QD-NEVPT2 results. Furthermore, we tested its applicability to a large photoisomerization system using the green fluorescent protein model and the 10-state calculation of the large transition metal complex, showcasing that off-diagonal elements can be evaluated at a relatively low cost.

Keywords: quasi-degenerate perturbation theory; pair-natural orbitals; localized virtual molecular orbitals; excited states; secondorder *N*-electron valence state perturbation theory

I. Introduction

The incorporation of multireference (MR) character is important when modeling chemical reactions involving the formation or cleavage of covalent bonds. Moreover, various chemical species, such as doubly excited states and low-spin open-shell species with antiferromagnetically coupled electron pairs, exhibit strong MR character. The complete-active space self-consistent field (CASSCF) theory^{1,2} can capture the static correlation, thus providing a good zerothorder description of such complicated electronic states. By considering the dynamic electron correlation, MR perturbation theoretical (MRPT) approaches often provide quantitative accuracy for various phenomena. The most widely-used variants of MRPT schemes involve the complete-active space perturbation theory (CASPT2) and N-electron valence state perturbation theory (NEVPT2) methods pioneered by Roos et al.³⁻⁵ and by Angeli et al.,^{6,7} respectively, as well as the MR Møller-Plesset perturbation (MRMP) by Hirao⁸ and multi-configurational quasi-degenerate perturbation theory (MC-QDPT) by Nakano⁹.

The CASPT2 scheme is among the first MRPT methods based on the so-called internally-contracted basis (ICB) functions¹⁰ and its reliability has been validated against various systems including transition metal^{11,12} and heavy metal^{13–15} systems, singletfission,¹⁶ active-site models of bio-mimetic systems^{17,18} to only name a few. Owing to the complete one-electron nature of the zerothorder Hamiltonian, the CASPT2 scheme is prone to the intruder-state problem (ISP), and thus suffers from small denominators in the perturbative energy expression. Accordingly, real¹⁹ and imaginary²⁰ level-shifting techniques have been developed. The imaginary shift in the CASPT2 method can be regarded as a diagonal Thikonov regularization,²¹ which shifts the singularity towards the imaginary axis. Recently, the so-called σ^p -regularization^{22,23} was introduced to remove the ISP from the CASPT2 framework.²⁴ Another type of modifications in zeroth-order Hamiltonian focus on a more balanced treatment between closed-shell and open-shell configurations in the CASPT2 scheme. The ionization potential and electron affinity (IPEA) shift introduces an empirical shift parameter in the CASPT2 denominator.²⁵

The complete two-electron interactions inside the active space are treated at the zeroth-order level in the NEVPT2 method by employing Dyall's Hamiltonian²⁶ as the zeroth-order part. Consequently, the NEVPT2 scheme is considered less susceptible to ISP, or is often regarded as an ISP-free method.²⁷ A fully internally-contracted (FIC)-NEVPT2 computation requires a full diagonalization of Dyall's Hamiltonian matrix over ICBs. A simpler, diagonalization-free variant called the strong-contraction (SC) scheme⁷ has been proposed to alleviate this step. On a side note, to effectively take into account the two-electron interactions at the zeroth-order level in the CASPT2 scheme, Kollmar and co-workers developed the so-called CASPT2-K scheme,²⁸ which uses a shift parameter determined using the Dyall's Hamiltonian.

Modeling the photo-chemical processes often requires electronic structure computations on ground- and excited-state potential energy surfaces (PESs) to locate the minimum, the conical intersection (CI), and the avoided-crossing (AC) states. Conventional single-state perturbative methods, such as state-specific (SS)-CASPT2 and NEVPT2, are often insufficient for constructing a correct wave function representation around the CI or AC, where multiple PESs become near-degenerate. In fact, the coupling of near-degenerate states are properly taken into account using a perturbative expansion of an effective Hamiltonian matrix,^{29–32} which is known as quasi-degenerate perturbation theory (QDPT). The QDPT variant

of CASPT2 approach was originally pioneered by Finley *et al.*³³ as the multi-state (MS)-CASPT2 scheme. The extended multi-state (XMS)-CASPT2 scheme was developed by Shiozaki *et al.*³⁴ to guarantee the invariance to reference rotations in a similar vein to the extended MC-QDPT approach by Granovsky.³⁵ Along a similar line, the QD-NEVPT2 scheme^{27,36} was formulated for both FIC and SC schemes.

Numerous attempts have been made to accelerate the MRPT computations. Aquilante *et al.* introduced frozen-natural orbital (FNO) truncation in the CASPT2 method^{37–39} combined with the Cholesky decomposition of electron repulsion integrals (ERIs).^{40–43} Song and Martínez developed a tensor hyper-contraction-based (THC)-CASPT2 scheme and the XMS variant, and further extended them to analytical energy gradient computations.^{44–46}

A further compaction of ERIs as well as many-body amplitudes was achieved by exploiting the underlying locality of the electronic wave function.^{47–49} Guo *et al.* developed a domain-based local pairnatural orbital implementation of the NEVPT2 scheme, termed as the DLPNO-NEVPT2 method, and demonstrated its applicability to MR systems comprising hundreds of atoms and thousands of atomicorbital (AO) basis functions.⁵⁰ The concept of local PNOs was introduced to SS- and MS-CASPT2 schemes by Kats *et al.*^{51,52} on a virtual machine framework for sparse tensor objects.⁵³ Recently, we developed the PNO-CASPT2 and NEVPT2 schemes using orthonormal localized virtual molecular orbitals (LVMOs) in place of traditional projected atomic orbitals (PAOs) as an intermediate local basis.^{54,55}

The concept of local correlation was realized in the 1960s,^{47,48} and the actual computer implementation was first achieved by Pulay *et al.* in the 1980s.^{49,56,57} Combined with the domain selection algorithm by Boughton and Pulay⁵⁸ as well as Werner, Schütz, Manby and co-workers developed local versions of Møller–Plesset (MP) and coupled-cluster (CC) approaches and implemented them into efficient computer codes.^{59–65} Later, the concept of PNOs was reintroduced by Neese *et al.* in the local PNO-based coupled-electron pair approximation (LPNO-CEPA)⁶⁶ and CC with singles and doubles (LPNO-CCSD) schemes^{67–71} with full exploitation of resolution-of-the-identity (RI) approximation of ERIs.^{72–74} The idea of PNO framework was initially pioneered in the 1960s so as to effectively truncate the configuration expansion of many-electron wave functions.^{75–83}

To further reduce the number of RI integrals for computation, the locality of the wave function was fully utilized in the PNObased CC schemes, resulting in the development of the DLPNO-CC method.^{84,85} The initial DLPNO-CC implementation exhibited a desirable near-linear scaling behavior for linear one-dimensional systems and was applicable to Crambin, a small protein comprising more than 600 atoms. The PNOs for diagonal pairs are often referred to as orbital-specific virtuals (OSVs),86-88 and OSV-based local CC programs were developed.^{89,90} The DLPNO algorithm was further improved using the so-called sparse map framework,^{91,92} and was extended to property computations, 93-95 open-shell species, 96explicit correlation,^{97–99} and analytical energy gradient.^{100,101} In a similar vein, efficient local PNO-based MP and CC schemes were formulated and implemented by Werner et al.¹⁰²⁻¹¹⁰ On a footnote, by using different sets of truncation thresholds for pairs belonging to different fragments, multilevel (ML) treatment has been rendered available at the DLPNO-CC level.¹¹¹ When tracing a reaction profile using ML-DLPNO approaches, the selection of orbital pairs is crucial for the accurate calculation of the relative energies.^{112,113}

Reduced-scaling excited-state methods are particularly important in photochemistry. For such purpose, the local versions of CC approaches have been extended to the excited states.^{114–116} The second-order CC (CC2) and algebraic diagrammatic construction (ADC(2)) schemes were formulated in the PNO basis.^{117–119} Nooijen's similarity-transformed equation-of-motion (STEOM) approach^{120–122} was incorporated into DLPNO framework using either back-transformed PNO amplitudes for the ground state¹²³ or fully PNO-based ionization-potential (IP)¹²⁴ and electron affinity (EA)¹²⁵ EOM machineries.¹²⁶

The MR character is often more pronounced in the excited states. From this perspective, reduced-scaling MR-QDPT approaches such as the PNO-MS-CASPT2⁵² and THC-XMS-CASPT2⁴⁵ schemes are of central importance as versatile tools for exploring the PESs of various electronic states. However, to the best of our knowledge, reduced-scale NEVPT2 schemes have not yet been extended to QDPT variants. This motivated us to develop the PNO-QD-NEVPT2 method for the accurate photochemical modeling of large, real-life systems.

In a PNO-based wavefunction computation, the construction of the Fock operators and local RI 3-index integral transformation are often the most time-consuming steps. Therefore, to minimize such steps, in our PNO-QD-NEVPT2 formalism, a single set of LMOs/LVMOs was used to solve the SS-PNO-NEVPT2 equations and off-diagonal couplings in the effective Hamiltonian. Meanwhile, as a zeroth-order Hamiltonian, the state-specific Dyalls Hamiltonian was used instead of the state-averaged counterpart.

In the process of developing and benchmarking the PNO-QD-NEVPT2 scheme, we realized that the ISP is a common issue in NEVPT2 calculations for higher-lying states, even without local truncation. Numerical analysis revealed that ISPs in the canonical and PNO-NEVPT2 schemes likely arose from a semi-internal ICB manifold $(V(-1')_a$ subspace) and can easily be remedied by using the well-known imaginary shift, with no notable increase in computational costs. Moreover, by evaluating the Hylleraas functional only for that subspace using the converged NEVPT2 amplitudes with the level shift, the full NEVPT2 energies can be recovered for those states.

The remainder of this study is organized as follows. In Sec. II, we present a brief summary of the LVMO-based PNO formalism and the local RI 3-index integral generation algorithm using LMOs and LVMOs. Off-diagonal elements in the PNO-QD-NEVPT2 effective Hamiltonian were formulated by inserting a projection operator into a state-specific ICB manifold. With this choice, an off-diagonal element term was written as the product of the right-hand side (RHS), PNO-NEVPT2 amplitudes, and interreference ICB and PNO overlap matrices. The former two quantities were computed and stored in the PNO-NEVPT2 computations for diagonal elements, whereas the remaining off-diagonal elements were easily constructed on-thefly with negligible costs. In Sec. III, the accuracy of the PNO-QD-NEVPT2 scheme was benchmarked for small organic molecules, and the impact of ISP was assessed. The photoisomerization profiles of the silepin derivatives were computed at the PNO-OD-NEVPT2 level and compared with the canonical variant. To demonstrate its applicability to large real-life systems, the PNO-QD-NEVPT2 scheme was applied to a green fluorescent protein (GFP) model system and large transition metal complexes. The largest was composed of 4,200 AOs with a triple-zeta basis set. Finally in Sec. IV, conclusions are drawn.

II. Theory

In this section, we will start by providing a brief introduction to the conventional QD-NEVPT2 theory. We then discuss our new approaches to accelerate it using the PNO method and local RI algorithms. We also provide a brief review of the domain construction scheme that we developed in our previous work.^{54,55} In addition, we present a level-shift method for NEVPT2 to mitigate the ISP found in excited-state calculations. Unless otherwise mentioned, the same notation for the indices was used, as in a previous study [Ref. 55].

A. QD-NEVPT2 Theory

The QD-NEVPT2 theory was developed as an extension of the original NEVPT2 theory⁷ to the multi-state (MS) regime. It was developed based on the multipartitioning quasidegenerate perturbation theory,¹²⁷ wherein the electronic Hamiltonian is divided into the state-specific zeroth-order Hamiltonian and perturbation terms as follows:

$$H = H_{\alpha}^{(0)} + V_{\alpha} \quad (\alpha = 1, 2, \cdots, N),$$
 (1)

where α represents the reference index. In the NEVPT2 theory, the Dyall Hamiltonian,²⁶ denoted $H_{\alpha}^{\text{Dyall}}$, is employed as the zeroth-order Hamiltonian,

$$H_{\alpha}^{(0)} = P H_{\alpha}^{\text{Dyall}} P + Q H_{\alpha}^{\text{Dyall}} Q.$$
 (2)

The operator *P* is a projector for the model space spanned by the reference CASSCF wave functions $\Psi_{\alpha}^{(0)}(\alpha = 1, 2, \dots, N)$

$$P = \sum_{\alpha}^{N} |\Psi_{\alpha}^{(0)}\rangle \langle \Psi_{\alpha}^{(0)}|, \qquad (3)$$

and the complementary projector Q is expressed as

$$Q = 1 - P. \tag{4}$$

The Dyall Hamiltonian comprises three terms,

$$H_{\alpha}^{\text{Dyall}} = H_{\alpha}^{\text{inact}} + H^{\text{act}} + C_{\alpha} \,. \tag{5}$$

The terms $H_{\alpha}^{\text{inact}}$ and H^{act} are defined as

$$H_{\alpha}^{\text{inact}} = \sum_{ij} F_{ij,\alpha} E_j^i + \sum_{ab} F_{ab,\alpha} E_b^a \,, \tag{6}$$

$$H_{\rm act} = \sum_{pq} h_{pq}^{\rm core} E_q^p + \frac{1}{2} \sum_{pqrs} (pr|qs) E_{rs}^{pq}, \qquad (7)$$

with the one-electron core Hamiltonian h_{pq}^{core} given as

$$h_{pq}^{\text{core}} = h_{pq} + \sum_{i} [2(pq|ii) - (pi|iq)].$$
 (8)

Eq. (6) encompasses the generalized Fock matrix $F_{xy,\alpha}$ as a function of the state α , which is written as

$$F_{xy,\alpha} = h_{xy}^{\text{eff}} + \sum_{pq} [(xy|pq) - \frac{1}{2}(xp|yq)]D_{q,\alpha}^{p}, \qquad (9)$$

where $D_{q,\alpha}^p$ are elements of the one-body reduced density matrix (1-RDM). The C_{α} in Eq. (5) is defined as follows:

$$C_{\alpha} = \sum_{i} h_{ii} + \sum_{ij} [2(ii|jj) - (ij|ij)] - 2\sum_{i} F_{ii,\alpha}.$$
 (10)

This zeroth-order construction allows the CASSCF wave functions to form as eigenfunctions of the Dyall Hamiltonian:

$$H_{\alpha}^{\text{Dyall}} |\Psi_{\alpha}^{(0)}\rangle = E_{\alpha}^{(0)} |\Psi_{\alpha}^{(0)}\rangle , \qquad (11)$$

where the eigenvalues $E_{\alpha}^{(0)}$ correspond to the associated CASSCF energies.

Two variants exist for the multiroot treatment of the QD-NEVPT2 theory: the state-specific (SS) and state-average (SA) schemes.¹²⁸ They primarily differ in the 1-RDMs, $D_{q,\alpha}^p$, used to evaluate the generalized Fock matrix $F_{xy,\alpha}$ (Eq. (9)); the SS-RDMs and SA-RDMs are used for the SS and SA schemes, respectively, and the resulting $F_{xy,\alpha}$ are designated as SS and SA generalized Fock matrices, respectively. We employed the SS scheme in this study; thus, the 1-RDM elements were evaluated as $D_{q,\alpha}^p = \langle \Psi_{\alpha}^{(0)} | E_q^p | \Psi_{\alpha}^{(0)} \rangle$. The multipartitioning technique developed by Zaitsevskii and Malrieu is fundamental to treating the state-specific zeroth-order Hamiltonians.

Let us consider the following model-space states $\tilde{\Psi}_{\alpha}$, which are obtained by applying *P* to the exact wave functions Ψ_{α} , as:

$$\tilde{\Psi}_{\alpha} = P \Psi_{\alpha} \,. \tag{12}$$

We introduce the wave operator Ω , which offers the exact wave functions Ψ_{α} when acting on $\tilde{\Psi}_{\alpha}$ as follows:

$$\Omega \tilde{\Psi}_{\alpha} = \Psi_{\alpha} \,. \tag{13}$$

In the framework of the QDPT, the operator Ω can be determined as a solution for the generalized Bloch equation¹²⁹

$$\Omega PH\Omega - H\Omega = 0. \tag{14}$$

The following entity is defined as the effective Hamiltonian

$$H_{\rm eff} = PH\Omega. \tag{15}$$

Now, we express the wave operator Ω and the effective Hamiltonian H_{eff} in the perturbation expansion as

$$\Omega = P + \Omega^{(1)} + \Omega^{(2)} + \cdots$$
 (16)

and

$$H_{\rm eff} = H_{\rm eff}^{(0)} + H_{\rm eff}^{(1)} + H_{\rm eff}^{(2)} + \cdots$$
(17)

respectively. Substituting these expansions into Eq. (14) yields the following second-order effective Hamiltonian $H_{\rm eff}^{2nd}$, which is expressed using the first-order wave operator $\Omega^{(1)}$ as:

$$H_{\rm eff}^{\rm 2nd} = H_{\rm eff}^{(0)} + H_{\rm eff}^{(1)} + H_{\rm eff}^{(2)}$$

= PHP + PHQ⁽¹⁾P. (18)

The central tasks of the QD-NEVPT2 calculation are twofold: (1) the SS-based determination of the first-order perturbations to the reference wavefunctions and (2) the evaluation of the diagonal and offdiagonal matrix elements of $H_{\rm eff}^{2nd}$ in the reference state basis.

Next, we describe the formulae for evaluating $H_{\rm eff}^{2nd}$ in the QD-

NEVPT2 approach. Diagonal elements of $H_{\text{eff}}^{2\text{nd}}$ correspond to the SS-NEVPT2 energies $E_{\alpha}^{2\text{nd}}$ as follows:

$$\langle \Psi_{\alpha}^{(0)} | H_{\text{eff}}^{\text{2nd}} | \Psi_{\alpha}^{(0)} \rangle = E_{\alpha}^{\text{2nd}}, \qquad (19)$$

where the PT2 energy for the α -th state is calculated to be $E_{\alpha}^{(2)} = \langle \Psi_{\alpha}^{(0)} | H | \Psi_{\alpha}^{(1)} \rangle$. The off-diagonal elements are expressed as

$$\langle \Psi_{\beta}^{(0)} | H_{\text{eff}}^{2\text{nd}} | \Psi_{\alpha}^{(0)} \rangle = \langle \Psi_{\beta}^{(0)} | H \Omega^{(1)} | \Psi_{\alpha}^{(0)} \rangle$$

$$= \langle \Psi_{\beta}^{(0)} | H | \Psi_{\alpha}^{(1)} \rangle .$$

$$(20)$$

The first-order wave functions $\Psi_{\alpha}^{(1)}$ are determined by solving the first-order equation:

$$\left(H_{\alpha}^{\text{Dyall}} - E_{\alpha}^{(0)}\right) \left|\Psi_{\alpha}^{(1)}\right\rangle = -\left(V_{\alpha} - E_{\alpha}^{(1)}\right) \left|\Psi_{\alpha}^{(0)}\right\rangle.$$
(21)

Eq. (21) is solved via the expansion of $\Psi_{\alpha}^{(1)}$ into eight types of non-redundant ICB sets (nrICBs),

$$\begin{split} \Psi_{\alpha}^{(1)} \rangle &= \sum_{i \leq j} \sum_{ab} t_{ab,\alpha}^{ij} |\Phi_{ij,\alpha}^{ab}\rangle \\ &+ \sum_{\rho_{(-1)}i} \left[\sum_{a \leq b} t_{ab,\alpha}^{\rho_{(-1)}i} |\tilde{\Phi}_{\rho_{(-1)}i,\alpha}^{ab}\rangle + \sum_{a < b} t_{ab,\alpha}^{\prime\rho_{(-1)}i} |\tilde{\Phi}_{\rho_{(-1)}i,\alpha}^{\prime ab}\rangle \right] \\ &+ \sum_{\rho_{(-2)}} \sum_{ab} t_{ab,\alpha}^{\rho_{(-2)}} |\tilde{\Phi}_{\rho_{(-2)},\alpha}^{ab}\rangle + \sum_{i\rho_{(0')}} \sum_{a} t_{a,\alpha}^{i\rho_{(0')}} |\tilde{\Phi}_{i\rho_{(0')},\alpha}^{a}\rangle \\ &+ \sum_{\rho_{(+1)}a} \left[\sum_{i \leq j} t_{\rho_{(+1)}a,\alpha}^{ij} |\tilde{\Phi}_{ij,\alpha}^{\rho_{(+1)}a}\rangle + \sum_{i < j} t_{\rho_{(+1)}a,\alpha}^{\prime ij} |\tilde{\Phi}_{ij,\alpha}^{\prime\rho_{(+1)}a}\rangle \right] \\ &+ \sum_{\rho_{(-1')}} \sum_{a} t_{a,\alpha}^{\rho_{(-1')}} |\tilde{\Phi}_{\rho_{(-1')},\alpha}^{a}\rangle + \sum_{i j} \sum_{\rho_{(+2)}} t_{\rho_{(+2)}a}^{ij} |\tilde{\Phi}_{ij,\alpha}^{\rho_{(+2)}}\rangle \\ &+ \sum_{i} \sum_{\rho_{(+1')}} t_{i,\alpha}^{\rho_{(+1')}} |\tilde{\Phi}_{i,\alpha}^{\rho_{(+1')}}\rangle, \end{split}$$
(22)

where $|\Phi_{ij}^{ab}\rangle$, $|\tilde{\Phi}_{\rho_{(-1)}i}^{ab}\rangle$, $|\tilde{\Phi}_{\rho_{(-2)}}^{ab}\rangle$, $|\tilde{\Phi}_{i\rho_{(0')}}^{a}\rangle$, $|\tilde{\Phi}_{ij}^{\rho_{(+1)a}}\rangle$, $|\tilde{\Phi}_{\rho_{(-1')}}^{a}\rangle$, $|\tilde{\Phi}_{ij}^{\rho_{(+2)}}\rangle$, and $|\tilde{\Phi}_{i}^{\rho_{(+1)}}\rangle$ —where the state index α is omitted—correspond to the nrICBs for the subspaces $S_{ij,ab}^{(0)}$, $S_{i,ab}^{(-1)}$, $S_{ab}^{(-2)}$, $S_{i,a}^{(0')}$, $S_{ij,a}^{(+1)}$, $S_{a}^{(-1')}$, $S_{ij}^{(+2)}$, and $S_{i}^{(+1')}$, respectively. The eight types of amplitudes, t_{ab}^{ij} , $t_{ab}^{\rho_{(-1)}i}$, $t_{ab}^{\rho_{(-1)}i}i$, $t_{ab}^{\rho_{(-1)}i}i$, $t_{ab}^{\rho_{(-1)}i}i$, $t_{ab}^{\rho_{(-1)}i}i$, $t_{ab}^{\rho_{(-1)}i}i$, $t_{$

Tangible expressions of the nrICBs have been shown in previous studies, including the original study.^{7,54,55} For example, the nrICBs for the subspace $S_{ab}^{(-2)}$ were constructed based on the following generalized eigenvalue equation:

$$K_{\alpha}X_{\alpha} = -D_{2,\alpha}X_{\alpha}e_{\alpha}, \qquad (23)$$

where $D_{2,\alpha}$ is the two-body RDM (2-RDM), the eigenvector matrix X_{α} is used to form the nrICBs, and the eigenvalues e_{α} are the associated energies. The Koopmans matrix K_{α} is given as

$$K_{rs,\alpha}^{pq} = \langle \Psi_{\alpha}^{(0)} | E_{ab}^{pq} [H_{\text{act}}, E_{rs}^{ab}] | \Psi_{\alpha}^{(0)} \rangle .$$
⁽²⁴⁾

Using the matrix X_{α} , the nrICBs $|\tilde{\Phi}^{ab}_{\rho_{(-2)},\alpha}\rangle$ are represented as follows:

$$|\tilde{\Phi}^{ab}_{\rho_{(-2)},\alpha}\rangle = \sum_{pq} X^{pq}_{\rho_{(-2)},\alpha} |\Phi^{ab}_{pq,\alpha}\rangle , \qquad (25)$$

where $|\Phi_{pq,\alpha}^{ab}\rangle$ are the non-orthonormalized redundant ICB (rICB). The rICBs are fundamental many-body bases in the IC multireference PT treatment and are obtained by applying the spin-free excitation generators E_{pq}^{ab} to the reference $|\Psi_{\alpha}^{(0)}\rangle$ as follows:

$$\Phi^{ab}_{pq,\alpha}\rangle = E^{ab}_{pq} |\Psi^{(0)}_{\alpha}\rangle .$$
⁽²⁶⁾

Determination of the amplitude $t_{ab,\alpha}^{\rho_{(-2)}}$ is equivalent to finding a stationary point of the Hylleraas functional

$$E_{\alpha}^{(2)} = 2 \langle \Psi_{\alpha}^{(1)} | H | \Psi_{\alpha}^{(0)} \rangle + \langle \Psi_{\alpha}^{(1)} | H_{\alpha}^{\text{Dyall}} - E_{\alpha}^{(0)} | \Psi_{\alpha}^{(1)} \rangle .$$
 (27)

When canonical molecular orbitals are used, the diagonal nature of the Fock matrix yields the formula for $t_{ab,\alpha}^{\rho_{(-2)}}$ in a closed form:

$$t_{ab,\alpha}^{\rho_{(-2)}} = -\frac{\langle \tilde{\Phi}_{\rho_{(-2)},\alpha}^{ab} | H | \Psi_{\alpha}^{(0)} \rangle}{\langle \tilde{\Phi}_{\rho_{(-2)},\alpha}^{ab} | H_{\alpha}^{\text{Dyall}} - E_{\alpha}^{(0)} | \tilde{\Phi}_{\rho_{(-2)},\alpha}^{ab} \rangle},$$
(28)

where the denominator in Eq. (28) can be rewritten in a simplified form as

$$\langle \tilde{\Phi}^{ab}_{\rho_{(-2)},\alpha} | H^{\text{Dyall}}_{\alpha} - E^{(0)}_{\alpha} | \tilde{\Phi}^{ab}_{\rho_{(-2)},\alpha} \rangle = \varepsilon_{a,\alpha} + \varepsilon_{b,\alpha} - e_{\rho_{(-2)},\alpha} \,. \tag{29}$$

The amplitude of this subspace $t_{ab,\alpha}^{\rho_{(-2)}}$ contributes to a segment of the SS-NEVPT2 energy, as evaluated using the energy formula $\sum_{\rho_{(-2)}} \sum_{ab} \langle \Psi_{\alpha}^{(0)} | H | \tilde{\Phi}_{\rho_{(-2)},\alpha}^{ab} \rangle t_{ab,\alpha}^{\rho_{(-2)}}$. These formulas indicate that the NEVPT2 energy can be calculated in a noniterative manner using canonical orbitals.

The evaluation of the single off-diagonal element in Eq. (20) is as expensive as computing the NEVPT2 energy. As the number of reference states (i.e., *N*) increases, the number of off-diagonal elements that must be computed increases quadratically, rendering the construction of the effective Hamiltonian a demanding task. To avoid this problem, we use a state-based RI approximation for these elements. This allowed them to be effectively represented using the overlap matrix between the ICB bases as a much simpler substitution. Considering the subspace $S_{ab}^{(-2)}$ as an example, the off-diagonal element is written using the state-based RI treatment as:

$$\langle \Psi_{\beta}^{(0)} | H | \Psi_{\alpha}^{(1)} \rangle^{(-2)}$$

$$= \sum_{\rho_{(-2)}} \sum_{ab} \langle \Psi_{\beta}^{(0)} | H | \tilde{\Phi}_{\rho_{(-2)},\alpha}^{ab} \rangle t_{ab,\alpha}^{\rho_{(-2)}}$$

$$\approx \sum_{\rho_{(-2)}} \sum_{ab} \sum_{\tau_{(-2)}} \langle \Psi_{\beta}^{(0)} | H | \tilde{\Phi}_{\tau_{(-2)},\beta}^{ab} \rangle \tilde{S}_{\rho_{(-2)},\alpha}^{\tau_{(-2)},\beta} t_{ab,\alpha}^{\rho_{(-2)}},$$
(30)

where the ICB overlap matrix $ilde{m{S}}$ is defined as

$$\tilde{S}^{\tau_{(-2)},\beta}_{\rho_{(-2)},\alpha} = \langle \tilde{\Phi}^{ab}_{\tau_{(-2)},\beta} | \tilde{\Phi}^{ab}_{\rho_{(-2)},\alpha} \rangle .$$
(31)

Notably, the term $\langle \Psi_{\beta}^{(0)} | H | \tilde{\Phi}_{\tau_{(-2)},\beta}^{ab} \rangle$ in Eq. (30) also arises as the RHS term of the first-order equation (Eq. (21)) solved in the preceding SS-NEVPT2 calculation step. Furthermore, the amplitudes $t_{ab,a}^{\rho_{(-2)}}$, were determined in the SS-NEVPT2 calculation. Therefore, these two numerical objects were obtained prior to the QD calculation step and stored in the high-speed memory. Their compressed representations, enabled by the PNO approach, enabled to significantly reduce storage demands. Consequently, the off-diagonal elements can be evaluated efficiently by retrieving data for these terms from memory,

thus avoiding the large cost of recalculating the RHS terms. Our implementation for off-diagonal elements requires extra computation of the ICB overlap between different references, which is of relatively low cost.

The effective Hamiltonian (Eq. (18)), derived from the generalized Bloch formalism with the intermediate normalization (Eq. (14)), is non-Hermitian. Symmetric matrices are preferred for numerical handling; thus, the QD-NEVPT2 variant based on the canonical Van Vleck¹³⁰ was used in this study. Then, the effective Hamiltonian is then expressed as

$$(H_{\rm eff}^{2nd})_{\alpha\beta} = E_{\alpha}^{(0)} \delta_{\alpha\beta} + \frac{1}{2} [\langle \Psi_{\beta}^{(0)} | H | \Psi_{\alpha}^{(1)} \rangle + \langle \Psi_{\alpha}^{(0)} | H | \Psi_{\beta}^{(1)} \rangle].$$
(32)

Ref. 130 presented the implementation of the hermitized QD-NEVPT2 formalism with the SC treatment, whereas this study implemented it based on the FIC scheme. The diagonalization of the matrix $H_{\text{eff}}^{2\text{nd}}$ yields the QD-NEVPT2 energy $E_{\kappa}^{\text{QD-NEVPT2}}$,

$$\sum_{\beta} (H_{\rm eff}^{\rm 2nd})_{\alpha\beta} U_{\beta\kappa} = U_{\alpha\kappa} E_{\kappa}^{\rm QD-NEVPT2}, \qquad (33)$$

where U are the normalized eigenvectors. The QD-NEVPT2 wave function for the κ -th state is expressed as

$$|\Psi_{\kappa}^{\text{QD-NEVPT2}}\rangle = \sum_{\alpha} U_{\alpha\kappa}(|\Psi_{\alpha}^{(0)}\rangle + |\Psi_{\alpha}^{(1)}\rangle).$$
(34)

Mixing the multiple references $\{|\Psi_{\alpha}^{(0)}\rangle\}$ and their perturbations $\{|\Psi_{\alpha}^{(1)}\rangle\}$ delivers the effective representation of quasi-degenerate states.

B. The LVMO domain construction and local RI algorithm

We briefly summarize the domain construction scheme for LV-MOs developed in our previous studies.^{54,55} To simplify the domain and integral generations, in our computer implementation, the active MOs were included in both occupied and virtual MO spaces, resulting in an overlap of MO subspaces as in the case of the open-shell DLPNO-CC formalism.⁹⁶ Hereafter, \tilde{i} and \tilde{a} represent the occupied and virtual LMO subspaces, respectively, both of which commonly include the active MOs.

A key quantity is the so-called differential overlap integrals (DOIs) between occupied and virtual LMOs;

$$\mathrm{DOI}_{\tilde{i}\tilde{a}} = \sqrt{\int_{\mathbb{R}^3} |\phi_{\tilde{i}}(\mathbf{r})|^2 |\phi_{\tilde{a}}(\mathbf{r})|^2 \, d\mathbf{r}}.$$
 (35)

The DOIs were first introduced by Pinski *et al.*⁹¹ as an approximation to Schwartz prescreening integral

$$\operatorname{SPI}_{\tilde{i}\tilde{a}} = \sqrt{(\phi_{\tilde{i}}\phi_{\tilde{a}}|\phi_{\tilde{i}}\phi_{\tilde{a}})}.$$
(36)

The LVMOs with larger value of DOI than TCutDOI with a given occupied LMO \tilde{i} constituted the LVMO domain for \tilde{i} . Thus, the $L(\tilde{i} \rightarrow \tilde{a})$ map was created.

The auxiliary basis was truncated using the fitting domain constructed using the following quantity

$$M_{\tilde{i}A} = \sum_{\mu \in A} C_{\mu \tilde{i}} [\mathbf{SC}]_{\mu \tilde{i}}$$
(37)

where **C** and **S** matrices represent the LMO coefficient and the AO overlap matrices, respectively. All the auxiliary basis functions centered on atom A were included in the fitting domain for \tilde{i} if $M_{\tilde{i}A}$ was larger than TCutMKNFit threshold. The fitting domain is represented as $L(\tilde{i} \rightarrow I)$ or equivalently $L(\tilde{i} \rightarrow A)$.

Special care must be taken for domains associated with active MOs; as the amplitude equations are solved in the nrICB representation, all the active MOs must share the same domain. Thus, a union of all the maps for the active MOs was evaluated and shared by each active MO as the universal active domain.

To perform the PNO-QD-NEVPT2 computations, the required RI integrals were limited to the following type:

$$(I|\tilde{i}\tilde{a}) = \sum_{\mu} C_{\mu\tilde{i}} \sum_{\nu} C_{\nu\tilde{a}} (I|\mu\nu).$$
(38)

The formal scaling of a straightforward RI 3-index transformation (Eq. (38)) is of $O(N^4)$. The dipole-based prescreening of *ij* pairs achieved a drastic speedup of local construction of $(I|\tilde{a}a)$ integrals. In fact, in Eq. (38), the Gaussian-type orbital (GTO) integrals and matrix multiplications associated with the AOs and MOs required only by the prescreened pairs were not required in the following computational steps. The whole sets of LVMOs and auxiliary basis for \tilde{i} needed at the following semi-local screening and the iterative PNO-NEVPT2 steps can be represented as

$$\hat{\mathbf{L}}(\tilde{i} \to \tilde{a}) = \bigcup_{\tilde{j} \in \text{survived } (i,j) \text{ list}} \mathbf{L}(\tilde{j} \to \tilde{a})$$
(39)

and

$$\mathbf{\hat{L}}(\tilde{i} \to I) = \bigcup_{\tilde{i} \in \text{survived } (i,j) \text{ list}} \mathbf{L}(\tilde{j} \to I),$$
(40)

respectively.

The LVMO-based local RI 3-index integral transformation closely resembled the sparse-map-based algorithm used in the DLPNO framework developed in Ref. 91. To reduce the number of GTO integrals to compute and the matrix multiplication operations with the MO coefficient matrices, the $L(\tilde{i} \rightarrow \mu)$ and $L(\tilde{i} \rightarrow \nu)$ maps were constructed by analyzing the occupied and virtual LMO coefficient matrices, respectively. Using these maps, the following maps were further formed;

$$\mathbf{\hat{L}}(I \to \mu) = \left[\mathbf{\hat{L}}(\tilde{i} \to I)\right]^{-1} \subset \mathbf{L}(\tilde{i} \to \mu), \tag{41}$$

$$\mathbf{\hat{L}}(I \to \mathbf{v}) = \left[\mathbf{\hat{L}}(\tilde{i} \to I)\right]^{-1} \subset \mathbf{\hat{L}}(\tilde{i} \to \tilde{a}) \subset \mathbf{L}(\tilde{a} \to \mathbf{v})$$
(42)

where $[\cdots]^{-1}$ and \subset represent inversion and chaining operations on maps, respectively. The local RI 3-index integral generations in the LVMO basis is presented in Algorithm 1.

Algorithm 1 Local RI 3-index integral transformation algorithm

1: // 1) Computation of transformed RI integrals 2: for $I \in \{auxiliary basis functions\}$ do for $\mu \in \mathbf{\hat{L}}(I \rightarrow \mu)$ do 3: for $v \in \hat{\mathbf{L}}(I \to v)$ do 4: 5: Compute $(I|\mu_I v_I)$ end for 6: 7: 8: end for $(I|\tilde{i}_{I}\tilde{a}_{I}) = \sum_{\mu_{I}} C_{\mu_{I}\tilde{i}_{I}} \left[\sum_{\nu_{I}} C_{\nu_{I}\tilde{a}_{I}}(I|\mu_{I}\nu_{I}) \right] // 2 \times \text{DGEMM operations}$ 9. Store $(I|\tilde{i}_I\tilde{a}_I)$ for I10: end for 11: // 2) Sorting of transformed integrals 12: for $i \in \{\text{occupied LMOs}\}$ do for $I \in \hat{\mathbf{L}}(i \to I)$ do 13: 14: Get $(I|\tilde{i}_I\tilde{a}_I)$ for I15: for $a \in \hat{\mathbf{L}}(i \to a)$ do if $a \notin I \hat{\mathbf{L}}(I \to a)$ then 16: continue end if 17. 18: 19: $(I_{\tilde{i}}|\tilde{i}\tilde{a}_{\tilde{i}}) = (I|\tilde{i}_{I}\tilde{a}_{I})$ 20: 21: 22: end for end for Store $(I_{\tilde{i}}|\tilde{i}\tilde{a}_{\tilde{i}})$ for i23: end for

C. LVMO-PNO-QD-NEVPT2 Theory

Our study proposed a new approach that combined the PNO scheme with the QD-NEVPT2 theory, extending its applicability towards large quasi-degenerate multireference systems. This is hereafter referred to as the PNO-QD-NEVPT2 theory. The LVMOs are used to approximate the pair function, pair energy, and pair density. To illustrate, in the subspace $S_{ij,ab}^{(0)}$, these terms are expressed as follows:

$$|\Psi_{ij,\alpha}\rangle = \sum_{a_{ij}b_{ij}} t^{ij}_{a_{ij}b_{ij,\alpha}} |\Phi^{a_{ij}b_{ij}}_{ij,\alpha}\rangle , \qquad (43)$$

and

(44)

$$(\mathbf{D}_{ij,\alpha})_{a_{ij}b_{ij}} = \langle \Psi_{ij,\alpha} | E_{b_{ij}}^{a_{ij}} | \Psi_{ij,\alpha} \rangle, \qquad (45)$$

respectively. As also discussed in Ref. 55, the PNOs $\{|\hat{a}_{ij}\rangle\}$ were obtained by diagonalizing the pair density matrix. Thus, they are represented by a linear combination of the LVMOs associated with the pair domain, as follows:

 $e_{ii\,\alpha} = \langle \Psi_{\alpha}^{(0)} | H | \Psi_{ii\,\alpha} \rangle \,,$

$$\left|\hat{a}_{ij,\alpha}\right\rangle = \sum_{a_{ij}} d^{ij}_{a_{ij}\hat{a}_{ij,\alpha}} \left|a_{ij}\right\rangle, \qquad (46)$$

where $|a_{ij}\rangle$ are canonicalized within the given LVMO subspace. The PNO coefficients $d_{a_{ij}\hat{a}_{ij,\alpha}}^{ij}$ and the occupied number $\eta_{\hat{a}_{ij,\alpha}}^{ij}$ are determined by solving the eigenvalue equation:

$$\mathbf{D}_{ij,\alpha}\mathbf{d}_{\hat{a}_{ij,\alpha}}^{ij} = \eta_{\hat{a}_{ij,\alpha}}^{ij}\mathbf{d}_{\hat{a}_{ij,\alpha}}^{ij}.$$
(47)

In the PNO-QD-NEVPT2 computation, we discarded the PNOs with their occupied numbers $\eta_{\hat{d}_{ij,\alpha}}^{ij}$ less than the threshold T_{CutPNO} . This truncation underlies efficient computation of local correlation. On an important note, the LVMOs and domains were state-averaged and -universal, whereas the PNOs were state-specific or uniquely defined as a function of the reference state α .

In our implementation of the PNO-NEVPT2 theory, the doubly

external subspaces $(S_{ij,ab}^{(0)}, S_{i,ab}^{(-1)}, S_{ab}^{(-2)})$ and the semi-internal subspace $(S_{ij,a}^{(-1)})$ were expanded using the PNO basis. The first-order wave function PNO-NEVPT1 can then be written as:

$$\begin{split} |\Psi_{\alpha}^{(1)}\rangle &= \sum_{i \leq j} \sum_{\hat{a}_{ij,\alpha}\hat{b}_{ij,\alpha}} t_{\hat{a}_{ij,\alpha}\hat{b}_{ij,\alpha},\alpha}^{ij} |\Phi_{ij,\alpha}^{\hat{a}_{ij,\alpha}\hat{b}_{ij,\alpha}}\rangle \\ &+ \sum_{\rho_{(-1)}i} \sum_{\hat{a}_{i\rho_{(-1)},\alpha} \leq \hat{b}_{i\rho_{(-1)},\alpha}} t_{\hat{a}_{i\rho_{(-1)},\alpha}\hat{b}_{i\rho_{(-1)},\alpha},\alpha}^{\rho_{(-1)}i} |\tilde{\Phi}_{\rho_{(-1)}i,\alpha}^{\hat{a}_{i\rho_{(-1)},\alpha}}\rangle \\ &+ \sum_{\rho_{(-2)}} \sum_{\hat{a}_{\rho_{(-2)},\alpha}\hat{b}_{\rho_{(-2)},\alpha}} t_{\hat{a}_{\rho_{(-2)},\alpha}\hat{b}_{\rho_{(-2)},\alpha},\alpha}^{\rho_{(-2),\alpha}} |\tilde{\Phi}_{\rho_{(-2)},\alpha}^{\hat{a}_{\rho_{(-2)},\alpha}}\rangle \\ &+ \sum_{i\rho_{(0')}} \sum_{a_{i\rho_{(0')}}} t_{i\rho_{(0')}}^{i\rho_{(0')}},\alpha} |\tilde{\Phi}_{i\rho_{(0')},\alpha}^{a_{i\rho_{(0')}}}\rangle + \sum_{i\leq j} \sum_{\rho_{(+1)}\hat{a}_{ij,\alpha}} t_{\rho_{(+1)}\hat{a}_{ij,\alpha},\alpha}^{ij} |\tilde{\Phi}_{ij,\alpha}^{\rho_{(+1)}\hat{a}_{ij,\alpha}}\rangle \\ &+ \sum_{i\rho_{(-1')}} \sum_{a_{\rho_{(-1')}}} t_{a_{\rho_{(-1')}},\alpha}^{\rho_{(-1')}},\alpha} |\tilde{\Phi}_{\rho_{(-1'),\alpha}}^{a_{\rho_{(-1')},\alpha}}\rangle + \sum_{ij} \sum_{\rho_{(+2)}} t_{\rho_{(+2)},\alpha}^{ij} |\tilde{\Phi}_{ij,\alpha}^{\rho_{(+2)}}\rangle \\ &+ \sum_{i} \sum_{\rho_{(+1')}} t_{i,\alpha}^{\rho_{(+1')}} |\tilde{\Phi}_{i,\alpha}^{\rho_{(+1')}}\rangle, \end{split}$$
(48)

where \hat{a}_{ij} , $\hat{a}_{i\rho(-1)}$, and $\hat{a}_{\rho(-2)}$ are the PNOs for the subspaces $S_{ij,ab}^{(0)}$, $S_{i,ab}^{(-1)}$, and $S_{ab}^{(-2)}$ respectively. In this study, we newly introduced the domain truncation in the subspaces $S_{i,a}^{(0')}$ and $S_a^{(-1')}$ compared with the previous work.⁵⁵

The PNO-NEVPT2 residuum for the α -th state is expressed as

$$r_{I,\alpha} = \langle \tilde{\Phi}_{I,\alpha} | H | \Psi_{\alpha}^{(0)} \rangle + \langle \tilde{\Phi}_{I,\alpha} | H_{\alpha}^{\text{Dyall}} - E_{\alpha}^{(0)} | \Psi_{\alpha}^{(1)} \rangle , \quad (49)$$

where *I* denotes the index of the eight nrICBs types. The converged $\Psi_{\alpha}^{(1)}$ satisfied the following, also called the amplitude equation,

$$r_{I,\alpha} = 0 \quad \forall I. \tag{50}$$

which served as a linear equation to determine $\Psi_{\alpha}^{(1)}$. The offdiagonal elements of the diagonal DOMO and LVMO blocks of the Fock matrix in arising in Eq. (50) can be non-zero. This led us to iteratively solve the amplitude equation. We used the preconditioned conjugated gradient (PCG) algorithm or direct inversion in the iterative subspace (DIIS) as iterative solvers.

In general, obtaining a converged solution using iterative methods is challenging. We experienced poor convergence in determining the solution to Eq. (50) for high-lying excited states, for instance, when calculating more than 20 states. This convergence issue arises even in the absence of local truncation. Thus, we focused on improving the condition of the linear equation. To mitigate the convergence issues, we used the canonicalized VMOs in the subspaces $S_{i,a}^{(0')}$ and $S_a^{(-1')}$ and the DOMOs in the subspace $S_i^{(+1')}$. The use of canonical orbitals altered the amplitude formulae in the subspaces $S_a^{(-1')}$ and $S_i^{(+1')}$ to the following closed forms:

$$t_{a_{\rho_{(-1')}},\alpha}^{\rho_{(-1')}} = -\frac{\langle \tilde{\Phi}_{\rho_{(-1')},\alpha}^{a_{\rho_{(-1')},\alpha}} | H | \Psi_{\alpha}^{(0)} \rangle}{\langle \tilde{\Phi}_{\rho_{(-1')},\alpha}^{a_{\rho_{(-1')},\alpha}} | H_{\alpha}^{\text{Dyall}} - E_{\alpha}^{(0)} | \tilde{\Phi}_{\rho_{(-1')},\alpha}^{a_{\rho_{(-1')},\alpha}} \rangle$$
(51)

and

$$t_{i,\alpha}^{\rho_{(+1')}} = -\frac{\langle \tilde{\Phi}_{i,\alpha}^{\rho_{(+1')}} | H | \Psi_{\alpha}^{(0)} \rangle}{\langle \tilde{\Phi}_{i,\alpha}^{\rho_{(+1')}} | H_{\alpha}^{\text{Dyall}} - E_{\alpha}^{(0)} | \tilde{\Phi}_{i,\alpha}^{\rho_{(+1')}} \rangle},$$
(52)

respectively, which can offer the amplitudes $t^{\rho_{(-1')}}_{a_{\rho_{(-1')}},\alpha}$ and $t^{\rho_{(+1')}}_{i,\alpha}$ in a non-iterative manner. The canonicalization of the LVMOs is carried out within the domain space in all the ICB subspaces. As for the DOMOs, the scaling of canonicalization was in the subspace $S_i^{(+1')}$ is $O(N^3)$, given that the number of active MOs is constant with respect to the system size. Due to the fact that the LVMOs in the $S_{i,a}^{(0')}$ subspace was canonicalized in the $\{i
ho_{(0')}\}$ domain, the canonicalization of DOMOs led to a complete breakdown of local nature of both VMOs and DOMOs. This resulted in a non-iterative $O(N^4)$ operation. Therefore, it was decided to canonicalize only the DO-MOs in the $S_i^{(+1')}$ subspace, while those in $S_{i,a}^{(0')}$ counterpart were left untouched, i.e., localized. Again, the amplitudes in the subspace $S_a^{(-1')}$ and $S_i^{(+1')}$ were non-iteratively obtained using Eqs. (51) and (52). However, in contrast to the canonical NEVPT2, the integrals in Eqs. (51) and (52) were calculated using the approach described in Sec. II B. Further, for Eq. (51), the virtual MOs were truncated within the domain. This canonicalization approach was found to be very effective in improving the convergence, thus facilitating the 30-state PNO-QD-NEVPT2 computations.

The major task in implementing the PNO-QD-NEVPT2 theory on top of the PNO-based SS-NEVPT2 program is the development of an additional module to evaluate the off-diagonal elements of H_{eff}^{2nd} (Eq. (32)). For example, in the subspace $S_{ab}^{(-2)}$, the off-diagonal elements are written as

$$\langle \Psi_{\beta}^{(0)} | H | \Psi_{\alpha}^{(1)} \rangle^{(-2)}$$

$$= \sum_{\rho_{(-2)}, \alpha} \sum_{\hat{a}_{\rho_{(-2)}, \alpha}} \sum_{\hat{\tau}_{(-2)}, \beta} \sum_{\hat{\tau}_{(-2), \beta}} \sum_{\hat{b}_{\tau_{(-2)}, \beta}} \sum_{\hat{b}_{\tau_{(-2)}, \beta}} \langle \Psi_{\beta}^{(0)} | H | \tilde{\Phi}_{\tau_{(-2)}, \beta}^{\hat{a}_{\tau_{(-2)}, \beta}, \hat{b}_{\tau_{(-2)}, \beta}} \rangle$$

$$\times \tilde{S}_{\rho_{(-2)}, \alpha}^{\tau_{(-2)}, \beta} S_{\hat{a}_{\rho_{(-2)}, \alpha}, \rho_{(-2)}, \alpha}^{\hat{\tau}_{(-2)}, \beta} S_{\hat{b}_{\rho_{(-2)}, \alpha}, \rho_{(-2)}, \alpha}^{\hat{b}_{\tau_{(-2)}, \beta}} t_{\hat{a}_{\rho_{(-2)}, \alpha}, \beta}^{\rho_{(-2)}, \beta} t_{\hat{a}_{\rho_{(-2)}, \alpha}, \alpha}^{\rho_{(-2)}, \beta},$$
(53)

where $S_{\hat{a}_{p(-2),\alpha}\rho(-2),\alpha}^{\hat{a}_{\tau(-2),\beta}\tau_{(-2),\alpha}\beta}$ is the element of the PNO overlap matrix between the α and β reference states and is obtained as a product of eigenvectors of pair density

$$S_{\hat{a}_{\rho(-2)},\alpha}^{\hat{a}_{\tau(-2)},\beta}\tau_{(-2)},\alpha} = \sum_{a} d_{a\hat{a}_{\tau(-2)},\beta}^{\tau_{(-2)}} d_{a\hat{a}_{\rho(-2)},\alpha}^{\rho_{(-2)}}.$$
(54)

Certain parts of the off-diagonal elements associated with the subspace $S_{ij,ab}^{(0)}$ vanished based on the state-based RI approximation (Eq. (30)) because the corresponding ICB overlap was zero.

As mentioned previously, our implementation used state-averaged LMOs that served as common bases across all reference states This condition enabled us to readily reuse the data arrays of the RHS terms and amplitudes to compute the off-diagonal (or state-coupling) elements (Eq. (30)). In our implementation, these data arrays were stored in memory and reused where needed to avoid redoing the computation. Importantly, the compression with the PNO basis representation is beneficial for significantly reducing the size of the data arrays, compared with the canonical QD-NEVPT2 case. As expressed in Eq. (30), H_{eff}^{2nd} was calculated using the ICB and PNO overlap matrices between different reference states. The preparation of

these matrices is an additional major step compared to the PNO-SS-NEVPT2 theory, but it is computationally rather facile. Therefore, the total computational time for the PNO-QD-NEVPT2 calculation did not differ significantly from that for PNO-SS-NEVPT2 calculation.

D. Imaginary shift for NEVPT2 theory

As mentioned earlier, the NEVPT2 theory is considered less susceptible to ISP or is often regarded as ISP-free. This consensus is based on the fact that NEVPT2 uses Dyalls Hamiltonian involving complete two-electron interactions as the zeroth order instead of the one-electron Fock matrix employed in the CASPT2 theory. However, the benchmark calculations presented in Sec. III C revealed that the critical ISP were obtained in the NEVPT2 calculations for high-lying excited states, even without using the PNO basis. The denominator analysis showed that severe instability was caused by perturbations in the subspace $S_a^{(-1')}$.

As introduced in a previous study addressing the ISP in the CASPT2 method,¹³¹ we employed the imaginary level shift (LS) for the NEVPT2 theory. In contrast to the CASPT2 method, the shift was introduced only to the subspace $S_a^{(-1')}$. This partial LS treatment was allowed because the different types of the ICBs were not coupled via the Dyall Hamiltonian H_{α}^{Dyall} . The imaginary LS of *i* ε was added to the Dyall Hamiltonian as follows:

$$H^{\text{Dyall}}_{\alpha} \to H^{\text{Dyall}}_{\alpha} + i\varepsilon Q.$$
 (55)

The use of the shifted zeroth-order Hamiltonian yields the amplitude formula in the subspace $S_a^{(-1')}$ to be rewritten as

$$t_{a,\alpha}^{\rho_{(-1')}} = -\frac{\langle \tilde{\Phi}^{a}_{\rho_{(-1')},\alpha} | H | \Psi^{(0)}_{\alpha} \rangle}{\langle \tilde{\Phi}^{a}_{\rho_{(-1')},\alpha} | H^{\text{Dyall}}_{\alpha} - E^{(0)}_{\alpha} + \frac{\varepsilon^{2}}{H^{\text{Dyall}}_{\alpha} - E^{(0)}_{\alpha}} | \tilde{\Phi}^{a}_{\rho_{(-1')},\alpha} \rangle} .$$
 (56)

The second-order energy was computed by inserting the regulated amplitude into the Hylleraas functional (Eq. (27)).

$$\begin{split} E_{\alpha}^{(2)} + &= \sum_{\rho_{(-1')}} \sum_{a} \left[2t_{a,\alpha}^{\rho_{(-1')}} \langle \tilde{\Phi}_{\rho_{(-1')},\alpha}^{a} | H | \Psi_{\alpha}^{(0)} \rangle \right. \\ &+ \sum_{\rho_{(-1')}'} \sum_{a'} t_{a,\alpha}^{\rho_{(-1')}} \langle \tilde{\Phi}_{\rho_{(-1')},\alpha}^{a} | H_{\alpha}^{\text{Dyall}} - E_{\alpha}^{(0)} | \tilde{\Phi}_{\rho_{(-1')},\alpha}^{a'} \rangle t_{a',\alpha}^{\rho_{(-1')}'} \langle 5 \rangle \end{split}$$

None of the subspaces other than $S_a^{(-1')}$ are affected by the shift; therefore, the effect of the shift was expected to be smaller.

III. Results and discussion

A. Computational details

We implemented a QD extension of the highly-scalable PNO-NEVPT2 theory coupled with the LVMO scheme in our in-house quantum chemistry program suite, ORZ. It was built upon the statespecific PNO-NEVPT2 computer program developed in the previous study.⁵⁵ Note that our PNO-NEVPT2 implementation used the FIC ansatz based on Eq. (48), although we do not explicitly mention this explicitly thereafter. The workflow of the PNO-QD-NEVPT2 implementation is sketched in Fig. 1. The truncation thresholds used to construct the PNOs and the related domains for the PNO-NEVPT2 and PNO-QD-NEVPT2 calculations were obtained from Ref. 55; however, the threshold $T_{CutDOIActive}$ was lowered to 5.0×10^{-3} from its previous value (7.0×10^{-3}) . The first-order power-of-secondmoment (PSM) method¹³² was employed throughout this study as a localization method. The frozen core approximation was used in all NEVPT2-based calculations. Unless otherwise stated, we used an imaginary level shift (LS) of $0.1 E_{\rm h}$ for the NEVPT2 calculations, as proposed in Sec. II D. In Secs. III E and III F, the PNO-QD-NEVPT2 calculation was performed on a single computer node with 52 central processing unit (CPU) cores of Intel[®] Xeon[®] Gold 5320 processors and 512 GB of core memory. The timings of a single PNO-QD-NEVPT2 calculation were measured in hybrid parallel execution using eight Message Passing Interface (MPI) processes and four OpenMP threads per process. The ORCA quantum chemistry package version 5.0.3¹³³ was used for the state-averaged CASSCF (SA-CASSCF), SC-NEVPT2, and QD-SC-NEVPT2 calculations. The CASSCF orbitals used in our PNO-(QD-)NEVPT2 calculations were obtained using ORCA.



FIG. 1. Flowchart for the PNO-QD-NEVPT2 implementation.

B. Performance of LVMO-based local RI integral transformation for linear systems

We applied the LVMO-based local RI algorithm to linear phenylalkane systems to reveal the scaling behavior. The geometries were obtained from Refs. 54 and 55. A computer node equipped with an AMD EPYCTM 7453 processor and 448 GB of physical memory was used without competing jobs. For all computations, 12 MPI processes and two OpenMP threads were employed. The def2-SVP orbital¹³⁴ and the def2/JK auxiliary basis sets¹³⁵ were used.

In our local RI algorithm, when generating maps for screening GTOs and matrix multiplication operations, active MOs were included in both occupied and virtual MO spaces. As addressed in Sec. II B, this choice greatly simplified the RI integral generation step, because a single type of 3-index integral was sufficient to compute the PNO-NEVPT2 energy and amplitude. To assess the effect of such an overlapping orbital space, the timings for the local integral generations for the CASSCF(6e,6o) and HF references are shown in Fig. 2.

In the CAS(6*e*,6*o*) case, the computational time for generating $(I|\tilde{i}\tilde{a})$ integral was reduced from $O(N^4)$ to $O(N^2)$ as a function of system size. This is consistent with the computational scaling of the integral transformation in the open-shell DLPNO-CCSD scheme,⁹⁶ which uses the overlapping orbital subspaces. In contrast, in the HF reference case, where there are no active MOs, the scaling is further lower than that in the CAS(6*e*,6*o*) case.



FIG. 2. Timings of local RI integral generations for (a) CASSCF(6e,6o) and (b) HF or CAS(0e,0o) references. The def2-SVP orbital and def2/JK auxiliary basis sets were used. The 1*s* orbitals of carbon atoms were frozen.

C. Accuracy of the PNO-QD-NEVPT2 method for small size organic molecules

In our previous study, we revealed that our ground-state LVMO-PNO-NEVPT2 implementation could recover more than 99.85% of the canonical NEVPT2 correlation energy and was applicable to systems comprising 200 or more atoms.⁵⁵ Our main interest was thus to confirm that the QD extension in conjunction with the PNO treatment can maintain reliability and applicability to a degree similar to the ground-state case. Herein, we focused on verifying the accuracy of the predicted excitation energies. For this purpose, benchmark calculations for the LVMO-based PNO-QD-NEVPT2 method were performed on 21 small organic molecules, which were also tested in Ref. 55. The structures in Ref. 51 were used. The vertical excitation energies of the low-lying singlet excited states were calculated using SS- and QD-NEVPT2 treatments. The following reference states were examined: 1, 2, 5, 10, 15, 20, 25, and 30. The SA-CASSCF references were prepared with the active space consisting of all the valence π and π^* MOs for all the benchmark systems except biphenyl. We used a reduced active space CAS(10e, 10o) for biphenyl to mitigate the high computational expense that arises from the computation of RDMs and transition RDMs (TRDMs) for the full- π CAS(12e,12o) treatment. In the QD-NEVPT2 and PNO-QD-NEVPT2 calculations, the 1s orbitals of all atoms except hydrogen were treated as frozen core. The aug-cc-pVDZ orbital basis¹³⁶ and corresponding JK-fit auxiliary basis¹³⁷ were used.

Fig. 3 displays the errors in the total energies of all the states predicted using the PNO-QD-NEVPT2 method as a function of the number of reference states considered in the MS treatment. The errors were measured relative to the predictions obtained using the canonical QD-NEVPT2 method. The values were found to be less than 0.04 eV in most cases. There was a slight tendency for the errors to increase with the number of states. Outliers were observed for cases using a small number of reference states; however, the maximum error was only 0.082 eV for the five-state tryptophan calculation.

We focused on the excitation energies, which were evaluated as relative energies compared with the ground-state total energies. Assessing their errors can provide insight into practical performance. Fig. 4 shows that the errors in the predicted excitation energies were lower than 0.02eV in almost all cases. The maximum error was 0.05 eV in the 30-state PNO-QD-NEVPT2 calculation for pyridoxine. The use of the PNO treatment had a lesser impact on the errors of the excitation energies compared with those of the total energies. This suggests that the preferable error cancellation occurred in the energy differences. Overall, the PNO approximation combined with the QD-NEVPT2 method resulted in only minor errors.

We focused on the impact of imaginary LS on the NEVPT2 predictions. Fig. 5 shows a heatmap of the minimum absolute values of the original, non-shifted denominator in the energy formula for the subspace $S_a^{(-1')}$ in the 30-state NEVPT2 calculations. The evaluated denominator is expressed as

$$\langle \tilde{\Phi}^{a_{\rho_{(-1')}}}_{\rho_{(-1')},\alpha} | H^{\text{Dyall}}_{\alpha} - E^{(0)}_{\alpha} | \tilde{\Phi}^{a_{\rho_{(-1')}}}_{\rho_{(-1')},\alpha} \rangle .$$
(58)

This heatmap indicates that without the imaginary LS, the absolute value of several denominators fell below $0.001 E_h$. These near-zero values (much smaller than the tested LS value) caused instability associated with the ISP. Notably, the higher-lying excited states were more likely to encounter small denominators and therefore suffer from ISP. Fig. S4 (Fig. S5) shows a heat map of the absolute differences between the SS-NEVPT2 energies with and without the imaginary LS for canonical basis (PNO basis); these energies serve as diagonal elements (eq. (57)). They clearly indicate that the imaginary LS had a substantial impact on the PT2 energies of the states lying above the 5-th states, which thus seem to exhibit the ISP. This observation is unprecedented, as the NEVPT2 theory is considered ISP-free and thus requires no LS treatment. Nonetheless, we also confirmed that the denominators were rarely small for the ground state and up to the five lowest-lying excited states, reflecting the re-

sistance of the NEVPT2 theory to ISP.



FIG. 3. Errors in the PNO-QD-NEVPT2 total energies (eV) for 21 organic molecules compared with the canonical version.



FIG. 4. Errors in the PNO-QD-NEVPT2 excitation energies (eV) for 21 organic molecules compared with the canonical version.

D. Accuracy of the PNO-QD-NEVPT2 method for the system with conical intersection

The QD or MS approach is crucial for studying near-degenerate states including conical intersections, avoided crossings, and *d-d* transitions. In such applications, the off-diagonal PT2 terms, that is, Eq. (20), plays a significant role and causes strong mixing between the SS-NEVPT2 states. We assessed the accuracy of the PNO-QD-NEVPT2 method for systems involving quasidegenerate states by calculating the S₀ and S₁ energies of the organic fluorescent 1,1-dimethyldibenzo[b,f] silepin, or silepin. Fig. 6 shows the chemical structure of silepin. The previous study predicted that this molecule undergoing photoisomerization can encounter CI state-crossing on the nonradiative decay pathway.¹³⁸ We used three types of optimized structures at the TDDFT/TDA level of theory, as shown in



FIG. 5. Minimum absolute value of the denominator (Eh) in the energy formula in subspace $S_a^{(-1')}$ of the NEVPT2 calculation without imaginary shift for the 30 singlet states.

Ref. 138. These structures were obtained in the Frank-Condon (FC), fluorescent (Flu), and conical intersection (Con) states. The S₀ and S₁ energy levels approached closely in the Con geometry, involving the twisting of the central C-C bond. The (PNO-)QD-NEVPT2 calculations were performed on top of the SA-CASSCF reference states, which were based on the previous calculations.¹³⁸ These SA-CASSCF wavefunctions were calculated considering ten states using (10*e*,10*o*) as the active space, denoted as 10SA-CASSCF(10*e*,10*o*). We employed the aug-cc-pVDZ (for C and H) and aug-cc-pV(D+d)Z for Si and used the corresponding JK-fit auxiliary basis.^{139–141}

The accuracy was examined by comparing the energies obtained from the canonical QD-NEVPT2 and PNO-QD-NEVPT2 calculations for the S_0 and S_1 states with those of the FC, Flu, and Con structures (Fig. 7). The energies shown in Fig. 7 are given relative to those of the S_0 state in the FC geometry. These relative energies were quantitatively consistency for the canonical QDNEVPT2 and PNO-QD-NEVPT2 predictions. Table I lists the vertical excitation energies of S_1 along with the errors between the canonical QD-NEVPT2 and PNO-QD-NEVPT2 results. Overall, the errors were sufficiently small, and the largest error was found to be as small as 0.016 eV for the structure Flu. The negligible error in the PNO-QD-NEVPT2 prediction for the Con structure (0.001 eV) indicates that our PNO treatment facilitated the evaluation of the off-diagonal terms of the QD-NEVPT2 theory with considerably small errors.



FIG. 6. Chemical structure of 1,1-dimethyldibenzo[b,f] silepin



FIG. 7. Relative energies (eV) for the ground (S_0) and first excited (S_1) states computed with QD-NEVPT2 and PNO-QD-NEVPT2 methods for 1,1-dimethyldibenzo[b,f] silepin.

TABLE I. Vertical excitation energies and errors (eV) between QD-NEVPT2 and PNO-QD-NEVPT2 methods for 1,1-dimethyldibenzo[b,f] silepin.

FC	Flu	Con
4.118	3.067	0.339
4.123	3.083	0.340
0.005	0.016	0.001
	FC 4.118 4.123 0.005	FCFlu4.1183.0674.1233.0830.0050.016

E. Performance of the PNO-QD-NEVPT2 method for large photochemical systems

Next, we discuss applicability checks toward large systems. As a benchmark, the PNO-OD-NEVPT2 method was applied to a green fluorescent protein (GFP) photoreceptor unit model. This GFP model comprised a 4-hydroxybenzylidene1,2dimethylimidazolinone (HBDI) chromophore and surrounding amino acids. Using UCSF Chimera¹⁴², hydrogen atoms were added to the structure named QM-5, as described in Ref. 45. The resulting molecular system is displayed in Fig. 8, comprising 291 atoms, and was treated quantum mechanically (QM) as a whole. PNO-QD-NEVPT2 calculations were performed to obtain the energy levels of the two lowest-lying singlet states, S₀ and S₁, for structures with three different percentages of GFP core isomerization: 0, 50, and 100 %. We used the def2-SVP basis set (2652 AO basis functions) and the corresponding JK-fit auxiliary basis set. CAS(4e,3o) was employed as the active space, as was similarly used in Ref. 45. For comparison, we also used the QD-SC-NEVPT2 method, which is a strongly contracted (SC) variant. This SC approach is based on a smaller set of perturber functions, facilitating a reduction in computational cost compared to the FIC-based NEVPT2 approach utilized in our study. However, it is important to note that the difference in costs between FIC and SC may not be significant in this test case because we used a small active space.

The plot in Fig. 9 shows the relative energies of the S_0 and S_1 states computed using the QD-SC-NEVPT2 and PNO-QD-NEVPT2 methods, along with the SA-CASSCF energies. The PNO-OD-NEVPT2 method produced results that were almost identical to those obtained using the QD-SC-NEVPT2 method. The vertical excitation energies are presented in Table II, which reveal that the errors between the two methods were less than 0.05 eV. In addition, these PNO-QD-NEVPT2 energies were in good agreement with the results obtained by the QM/MM calculation using the THC-XMS-CASPT2 theory.⁴⁵ This QM/MM calculation in Ref. 45 treated the structure QM-5 at the QM level based on THC-XMS-CASPT2/6-31G* and further considered the rest of the protein environment and water molecules at the MM level, which were discarded in our PNO-QD-NEVPT2 and QD-SC-NEVPT2 calculations. This result indicated that the QM-only model used in this study (Fig. 8) was sufficienly large to capture the quantitatively relevant protein effect on the excitation energies of the HBDI chromophore.

Table III compiles the detailed computational timings of the PNO-QD-NEVPT2 calculations for the S_0 and S_1 states of the QM-5 model, along with the calculated values of the dynamic correlation energy, as a function of the percentage of isomerization. As evident, the percentage correlation energy of the PNO-NEVPT2 method relative to the canonical NEVPT2 method was greater than 99.91 % in all cases. These results indicate that the diagonal elements in the effective QD-NEVPT2 Hamiltonian were accurately evaluated. The computational timings for the PNO-QD-NEVPT2 calculations were comparable across all isomerization percentages. In all the structures, the computation of the off-diagonal elements required considerably less time than the diagonal PNO-SS-NEVPT2 computation. This was owing to the fact that in our implementation, the RHS and amplitudes resulting from the PNO-SS-NEVPT2 calculation were stored and reused for the computation of the off-diagonal terms (Eq. (53)). Table IV shows that using the PNO method, the amplitude was compressed to approximately 0.004% of its canonical (or uncompressed) form, and thus can be readily stored in the high-speed memory storage.



FIG. 8. HBDI chromophore and around neighboring residues (291 atoms). The structure is from Ref.45 and hydrogen atoms were added.



FIG. 9. Relative energies (eV) for the ground (S_0) and first excited (S_1) states computed with SA-CASSCF, QD-SC-NEVPT2, and PNO-QD-NEVPT2 methods for the system in Fig. 8.

TABLE II. Vertical excitation energies (eV) with CASSCF, QD-SC-NEVPT2, and PNO-QD-NEVPT2 methods. The table also shows the QM/MM (with small QM) calculation results using CASSCF and THC-XMS-CASPT2 computed by Martínez and co-workers.⁴⁵

	0	50	100
CASSCF /def2-SVP	4.089	2.779	1.517
CASSCF /6-31G* (QM/MM) 45	4.107	2.801	1.163
QD-SC-NEVPT2 /def2-SVP	2.807	2.143	1.193
PNO-QD-NEVPT2 /def2-SVP	2.757	2.122	1.188
THC-XMS-CASPT2 /6-31G* (QM/MM) ⁴⁵	2.569	1.903	1.000

	The corres performed	ponding JK-fit au 1 with a compute 2s and 512 GB of	xiliary basis was e r node with 52 CPI core memory. The OpenMP three	employed. All th U cores of Intel [®] a 8 MPI processe ads.	e computations v Xeon [®] Gold 53 s were used with	vere 120 1 4			
Percentage of isomerization (%)		0			50			100	
	S ₀ sta	te S ₁	whole system	S ₀ sta	te S ₁	whole system	S ₀ stat	e S ₁	whole system
Total time Fock matrix construction (RI-JK) Orbital localizations RI-PNO integral transformation PNO-NEVPT2 solver (total): Formation of orthonormal ICBs Crude Screening PNO-NEVPT2 coupled-pair solver Diagonal SS Computations Off-diagonal QD Computations Off-diagonal QD Computations Constructing Local PNO Overlap matrices for $S^{(-1)}$ Constructing Local PNO Overlap matrices for $S^{(-1)}$	$\begin{array}{c} 1.41 \\ 0.00 \\ 0.79 \\ 0.62 \end{array}$	$\begin{array}{c} 1.51 \\ 0.00 \\ 0.79 \\ 0.72 \end{array}$	7.11 7.11 1.14 1.14 1.135 0.00 0.03 0.04 0.03 0.00 0.00 0.00	Compu 1.55 0.00 0.79 0.76	tational Times () 1.58 0.00 0.79 0.79	hour) 7.06 2.18 2.18 0.90 0.90 0.02 0.02 0.00 0.00 0.00 0.00	$\begin{array}{c} 1.52 \\ 0.00 \\ 0.73 \\ 0.73 \end{array}$	1.52 0.00 0.79 0.73	$\begin{array}{c} 6.77\\ 2.51\\ 0.34\\ 0.00\\ 0.02\\ 0.02\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\$
Reference CASSCF energy $[E^{(0)}+E^{(1)}]$ +6458	-0.349200	-0.198920	R	eference and Dy -0.251200	namic Correlatic -0.149083	on Energies (Eh)	-0.128781	-0.073022	
Correlation energy for strong-pairs $[E_{\text{strong}}]+20$	-0.151648	-0.200565		-0.172901	-0.197126		-0.195627	-0.207873	
Correlation energy for weak-pairs $[E_{weak}^{(2)}]$	-0.037384	-0.037444		-0.037375	-0.037390		-0.037152	-0.037102	
$E_{ m strong}^{(2)}+E_{ m weak}^{(2)}+20$	-0.189033	-0.238008		-0.210275	-0.234515		-0.232778	-0.244975	
Percentage Correlation Energy (%)	99.91	99.91		99.91	16.66		99.91	99.91	

TABLE III: Computational timings of the PNO-QD-NEVPT2 method and dynamic correlation energies for HBDI chromophore in GFP and surrounding residues in S₀ and S₁ states with CAS(4e, 3o) treatment as a function of the percentage of isomerization.

		whole system	2652 12911 133 380 380 2136		144400 2280
	100	ate S ₁		27 24 96 343.2 372.6 380.0 510.6	17920 1010 5000.279 0.187 0.0037
		S0 St		27 25 105 343.2 408.6 380.0 510.6	17922 1193 5000.279 0.188 0.0038
VOs), and also shown.		whole system	2652 12911 133 380 380 2136		144400 2280
al orbitals (nr- sion ratio are a	50	lte S1		26 25 119 342.8 402.2 356.0 505.5	17900 1233 5000.279 0.182 0.0036
nbers of PNOs, non-redundant virtu Memory of amplitude and compres		S ₀ St		26 26 118 342.8 368.6 356.0 505.5	17898 1061 5000.279 0.181 0.0036
		whole system	2652 12911 133 380 380 2136		144 400 2280
verage numbe are shown. Me	0	te S1		26 24 118 340.0 399.8 310.0 505.3	17974 1315 5000.279 0.178 0.0036
TABLE IV: A urvived pairs :		S ₀ sta		26 24 108 340.0 349.1 310.0	17978 1037 5000.279 0.176 0.0035
<u>s</u>	Percentage of isomerization (%)		<pre># of AO basis # of auxiliary basis # of finzen MOs # of DOMOs # of active MOs # of VMOs (full)</pre>	Average # of PNOs for $S^{(0)}$ pairs Average # of PNOs for $S^{(-1)}$ pairs Average # of PNOs for $S^{(-2)}$ pairs Average # of n-VOs in $S^{(0)}$ pair domains Average # of n-VOs in $S^{(-1)}$ pair domains Average # of n-VOs in $S^{(-2)}$ pair domains Average # of auxiliary AOs in $S^{(0)}$ fitting domains	 # of IJ pairs (full) # of PI pairs (full) # of survived IJ pairs # of survived PI pairs # of canonical amplitude (GB) # of PNO amplitude (GB) Compression ratio of amplitue (%)

PNO-QD-NEVPT2 Theory with LVMO Bases

F. Performance of the PNO-QD-NEVPT2 method for large transition metal complexes

In Ref. 50, Guo and co-workers⁵⁰ demonstrated the efficiency of DLPNO-NEVPT2 by applying it to large transition metal (TM) complexes with moderate active spaces using the def2-TZVP basis set. We tested our PNO-QD-NEVTP2 method on two TM complexes studied by Guo et al. involving a few hundred atoms: the iron complex $\text{FeC}_{72}N_2H_{100}^{143}$ and the nickel complex $\text{NiC}_{90}N_{20}H_{120}^{144}$. The structures taken from the study by Guo and co-workers⁵⁰ are shown in Fig. 10. The def2-TZVP and the corresponding JK-fit auxiliary basis sets were employed. The number of AO basis functions was 2939 (iron complex) and 4175 (nickel complex). The active spaces used were CAS(6e,5o) for the iron complex and CAS(8e, 5o) for the nickel complex. We calculated the 10 lowest-lying states for the singlet and triplet states of iron and nickel complexes, respectively, using the corresponding 10SA-CASSCF wave functions as references. For comparison, several variants of the NEVPT2 theory were tested at the SC-NEVPT2, SS-NEVPT2, and QD-SC-NEVPT2 levels with canonical orbitals as well as at the PNO-based SS-NEVPT2 level of theory.

The excitation energies of the two complexes are plotted in Fig. 11. The plots show that the canonical NEVPT2 and PNO-NEVPT2 methods have provided almost similar predictions. The maximum errors in the excitation energies of the iron and nickel complexes were 0.0071 and 0.0063 eV, respectively. Table S2 indicates that the PNO-NEVPT2 method recovered 99.85% or more of the canonical NEVPT2 dynamic correlation energy of the iron complex. For the Ni complex, 99.80% or more of the canonical NEVPT2 dynamic correlation energies were captured (Table S4). The energy spectra provided by the SCNEVPT2 and NEVPT2 methods appeared to be similar, presumably because of the use of small active spaces. The PNO-QD-NEVPT2 method yielded results that were consistent with the other QD results obtained using the QD-SC-NEVPT2 method. These findings suggest that, for these TM complexes, the PNO-QD-NEVPT2 method produced results with an accuracy comparable to that of the canonical QD-NEVPT2 method. A comparison of the results for PNO-NEVPT2 and PNO-QD-NEVPT2 indicated that the multi-state treatment had a noticeable effect on the spectrum of the iron complex, whereas this effect was minor for the nickel complex.

Tables S2 and S4 show that the computational times of the PNObased SS-NEVPT2 calculations for single states appeared to be stateindependent. Notably, only 2.3 and 1.6% of the total time was used to compute all the off-diagonal elements of the effective Hamiltonian matrix for the iron and nickel complexes, respectively. This small amount of computational time for off-diagonal elements is reflected in our approach in the implementation to avoid the recalculations of the intermediate terms, as discussed in Secs. II A and II C.

IV. Conclusion

As a computationally efficient multi-state MRPT approach, we developed the QD extension of the PNO-NEVPT2 scheme, which utilized the LVMO scheme for the underlying local orbital representation. Using the state-based RI treatment, we derived a decomposed formula for the off-diagonal elements of the effective Hamiltonian matrix using the PNO representation. This formula facilitated the efficient evaluation of the off-diagonal elements via the restored amplitudes and intermediates obtained in the PNO-SS-NEVPT2 calcula-

tion step. With the PNO basis representation, the amplitudes and intermediates were drastically compressed; therefore, the storage size of the required data did not limit the application.

Illustrative tests revealed that NEVPT2 calculations for obtaining highly excited states had critical instability issues associated with ISP, regardless of the use of the PNO method. This instability was unexpected, as NEVPT2 was considered to be ISP-free. The analysis of the SS-NEVPT2 energy contribution revealed that certain denominators in the higher-lying excited states could be very small in absolute value, whereas this was not observed in the ground state or a certain number of lowest-lying excited states. To mitigate the ISP, we introduced an imaginary LS into the NEVPT2 and PNO-NEVPT2 methods.

The LVMO-based implementation of the PNO-QD-NEVPT2 method has been proven to reproduce 99.8% or more of the canonical QD-NEVPT2 correlation energies for all computed excited states, including high-lying states. The maximum error in excitation energies was only 0.05 eV for the PNO-QD-NEVPT2 calculations across 30 states of 21 organic molecules. This level of accuracy was maintained even for the conical intersection structures of 1,1dimethyldibenzo[b,f] silepin, which served as quasi-degenerate test cases. We performed the PNO-QD-NEVPT2 calculations on the HBDI chromophore and the surrounding residues, comprising 291 atoms, in GFP as an example of a large-scale photochemical system. The results obtained using the PNO-QD-NEVPT2 method with the large QM treatment were comparable with those obtained using the QM/MM calculation with the THC-XMS-CASPT2 method.⁴⁵ To demonstrate its scalability, we performed the 10-state PNO-QD-NEVPT2 calculation on the iron (175 atoms) and nickel (231 atoms) complexes. The computational timing for the off-diagonal elements of the PNO-QD-NEVPT2 calculation were negligibly small compared with that of the PNO-SS-NEVPT2 calculation for the diagonal elements.

The search for chemically significant points on energetically competing potential surfaces necessitates the development of appropriate analytical nuclear gradients. The analytical nuclear gradient of the QD-NEVPT2 theory has been intensively studied in recent years. The introduction of a PNO extension to the QD-NEVPT2 analytical gradient is desirable.

Supplementary Material

Supplementary Material presents data regarding the errors in the total energies of the PNO-QD-NEVPT2 method relative to the QD-NEVPT2 method for each of the 21 molecules. Errors in the excitation energies are also compiled. The absolute values of the dynamic correlation energy errors between the canonical NEVPT2 method with the imaginary LS and canonical NEVPT2 method without imaginary LS are shown. Numerical data obtained using the PNO method are also presented. Active MOs for the GFP photoreceptor unit and two TM complexes are shown. Information on the TM complex calculations, including computational timings and dynamic correlation energies, is provided.

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FIG. 10. Molecular structures used for the calculations



FIG. 11. Excitation energies (eV) for (a) 10 singlet states for FeC₇₂N₂H₁₀₀ and (b) 10 triplet states for NiC₉₀N₂₀H₁₂₀.

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Data Availability Statement

Data supporting the findings of this study are available from the corresponding author upon request.

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