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Similarity-transformed perturbation theory on top of truncated local coupled cluster solutions: Theory and applications to intermolecular interactions.

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Abstract

Your correspondents develop and apply fully-nonorthogonal, local-reference perturbation theories describing non-covalent interactions. Our formulations are based on a Löwdin partitioning of the similarity-transformed Hamiltonian into a zeroth-order intramonomer piece (taking local CCSD solutions as its zeroth-order eigenfunction) plus a first-order piece coupling the fragments. If considerations are limited to a single molecule, the proposed intermolecular similarity-transformed perturbation theory (iSTPT) represents a frozen-orbital variant of the "(2)"-type theories shown to be competitive with CCSD(T) and of similar cost if all terms are retained. Different restrictions on the zeroth- and first-order amplitudes are explored in the context of large-computation tractability and elucidation of non-local effects in the space of singles and doubles. To accurately approximate CCSD intermolecular interaction energies, a quadratically-growing number of variables must be included at zeroth-order. **Keywords**: intermolecular interactions, coupled cluster, perturbation theory

I. INTRODUCTION

With the formal foundations well-established for the routine computation of a host of molecular properties in density-functional and wavefunction frameworks, quantum chemistry has undoubtedly emerged as a mature field with considerable predictive power in the past few decades[1]. These advances coupled to ever-increasing improvements in computing power have served to steadily shift its scope of applied focus to larger systems of molecular clusters, extended surfaces, and even solvated biomolecules. To this end, much emphasis has been placed on the development of low-scaling approximations to high-level model chemistries, e.g., RI/density-fitting[2–7] for two-electron integrals, explicitly-correlated F12/R12[8–16] formulations, spin-component-scaled Laplace-transformed[17,18], and rank-reducing tensor decompositions[19–27] in Möller-Plesset (MP) and coupled cluster (CC) methodology, hybrid QM/MM[28,29] embedding approaches, and domain fragmentation for low-scaling local correlation methods.

Chief among the observables for which these efforts at economization have proved essential are binding energies. Perhaps the most popular of non-supermolecular schemes is symmetry-adapted perturbation theory (SAPT),[30,31] a many-body generalization of Heitler-London theory that treats the two-body Hamiltonian as a perturbation to monomer wavefunctions complete to some order in MP theory, furnishing decomposable interaction energies directly, that is, without subtraction. It has seen immense development in wavefunction and DFT[32,33] flavors, and even extention to the realm of molecular clusters with the use of pairwise-additive many-body techniques[34–36]. Among the most sophisticated coupled cluster-level variants are the CCD+ST(CCD)[37,38] and SAPT(CCSD)[39–42] methods. The former computes dispersion by solving intermonomer ring-CCD equations on top of CCD monomers and treats singles and triples perturbatively, and has recently been treated in a reduced "natural" orbital representation[43]. The latter computes dispersion from frequency-dependent polarizabilities of CCSD-level monomer wavefunctions and adds non-iterative triples and quadruples. These methods have shown themselves to be very accurate when applied to two-body interactions, but extending SAPT in its purest form to non-pairwise-additive interactions has proved far from straightforward[34–36,44–47]. Other direct methods tackle the problem via ap-

plication of the many-body expansion (MBE) separating pairwise, three-body, and higher terms. The fragment MO method[48–51], many-overlapping-body[52], divide-and-conquer,[53–57] and incremental[58] approaches, for instance, have produced encouraging energetics for calculations on large clusters, and are generally amenable to large-scale parallelization. Moreover, low-order truncations can furnish surprisingly accurate results while obviously conferring huge computational savings.

Non-constructive/supermolecular techniques generally seek to recover a given level of canonical treatment of the supersystem by carving out domains defining individual correlation problems, oftentimes in localized orbital representations. Such approaches are motivated by the inherent locality of dynamical correlations, and thus, neglecting distant correlations should effect lower scaling of the supermolecular computation without forfeiting accuracy. Pulay[59] and Saebø[60–63] did the first seminal work in this field, developing an iterative MP2 scheme retaining only a *quadratic* number of domain-pair amplitudes but recovering more than 98% of the canonical correlation energy in a basis of localized occupied orbitals and a non-orthogonal, redundant set of atomic orbitals projected into the virtual space (termed PAOs). Their approach has since inspired the non-iterative fixed-domain dimers- (DIM) and triatomics-in-molecules (TRIM)[64,65] models for MP2-level correlation and a fourth-order triples model[66,67], the local coupled cluster methods[68–73] introduced by Werner and Schütz and developed by others, purely AO-based algorithms[74–77], and mixed CC-MBPT approaches[78–80]. Other local correlation methods similar in spirit to the MBE approaches eschew non-orthogonality and its attendant complications, e.g., linear-dependence, rank dilation, and retention of overlap integrals in the spin-orbital equations, opting instead for localized orthogonal orbitals and domain specification based on the relative locality of the occupied subspace, allowing straightforward use of standard-package codes and facile parallelization of completely independent (albeit sometimes overlapping) subdomain calculations. These include the divide-expand-consolidate approach[81–83], natural linear scaling coupled cluster[84,85], the clusters in molecules[86,87] method, and other higher-order methods[88,89].

In our view, some qualities a local correlation model should possess include:

- Simple, physically-motivated domain identification

- Monotonic convergence to the (upper-bound) untruncated/canonical correlation energy as the model space is augmented to full-rank

- A consistent treatment of occupied and virtual subspaces

- No use of empirical parameters or numerical tolerances

- Significant cost-savings relative to the canonical result while remaining accurate for *relative* energies

- Extension (at least in principle) to arbitrary correlation rank

- Guaranteed smoothness on the potential energy surface

In this work, we introduce a hierarchy of local correlation theories which we feel satisfies all of the above criteria. Guided by the ethos of perturbation theory, we assume that the intermolecular interaction energy is *substantially* smaller than the total energy. Making use of Löwdin partitioning[90–94], we define a zeroth-order wavefunction as the solution of truncated, non-orthogonal, molecule-centered coupled cluster equations of at most a quadratic number of variables, and treat the non-local excitations using second-order similarity transformed perturbation theory (STPT). Our reference determinant shall be built from absolutely-localized molecular orbitals (ALMOs)[95–100], determined as the variational solution of locally-projected (SCFMI) equations[95,96] constraining the coefficient matrix to be block-diagonal in the molecules. Such a reference has treated induction effects to infinite-order (or satisfied Brillouin's condition on-site), but remains an upper bound to canonical Hartree-Fock (HF), increasingly accurate as inter-site Brillouin matrix elements vanish, e.g., for interactions between insulators or interactions approaching the long range. The theory necessary to precisely specify our models is developed in Sec. II.

With a series of test applications, in Sec. III we explore the extent to which our models represent attractive non-iterative alternatives to canonical MP2 where an absence of higher-order terms is responsible for a poor description of dispersion[101,102]. First, we uncover general properties of our intermolecular STPT models as applied to elementary dispersion interactions, including the convergence behavior of the binding energy and terms on basis set extension, BSSE effects, and performance on application to small clusters. A discussion of intra- and intermolecular relaxations due to the interplay of orbital choice and single excitations entering in the correlation problem will follow. Next, we discuss potential tractability gains achieved on subspace orthogonalization. In a final assessment of the generality of our conclusions, we compute statistical errors on application to the A24[103] data set of various

non-covalent interactions. Our conclusions are summarized in Sec. IV.

II. THEORY

Coupled cluster (CC) theory is an exponential reformulation of the Schrödinger equation that, unlike its linear parent, remains size-extensive *after* truncation. The CC ground state, $|\Psi\rangle = e^{\hat{T}}|0\rangle$ is written as the action of a cluster operator, $\hat{T}$ on a single reference configuration, $|0\rangle$. The cluster operator generally contains amplitudes, $\mathbf{t}$, in the full Hilbert space of n-electron Slater determinants, $|\mathbf{h}\rangle = |0\rangle + |\mathbf{s}\rangle + |\mathbf{d}\rangle + |\mathbf{t}\rangle + |\mathbf{q}\rangle + ...$, where $|\mathbf{s}\rangle$ are single substitutions from $|0\rangle$, $|\mathbf{d}\rangle$ are doubles, and so forth. Substituting the CC ground state into the Schrödinger equation, premultiplying by $e^{-\hat{T}}$ and projecting with all $\langle\mathbf{h}|$, yields the exact ground state energy, E, and amplitudes, $\mathbf{t}$:

$$E = \langle 0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle = \bar{\mathbf{H}}_{00}, \text{ and} \tag{1}$$

$$\mathbf{0} = \langle\mathbf{h}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle = \bar{\mathbf{H}}_{\mathbf{h0}}, \tag{2}$$

where we have introduced the similarity-transformed Hamiltonian, $\bar{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$, and its matrix elements. Similarity transformations leave the eigenvalue spectrum of $\hat{H}$ unchanged, implying a coupled cluster solution of full rank n will be equivalent to full configuration interaction (FCI). Such a limit is obviously infeasible, so eqs.1 and 2 are generally treated in a small subspace of $|\mathbf{h}\rangle$, denoted as $|\mathbf{p}\rangle$, solving $\bar{\mathbf{H}}_{\mathbf{p0}} = \mathbf{0}$ for $\mathbf{t_p}$ and neglecting all projections onto the complementary space, denoted as $|\mathbf{q}\rangle$.

A. Similarity transformed perturbation theory

Viewing a solution to a standard low-rank CC problem in $|\mathbf{p}\rangle$ as a well-defined zeroth-order wavefunction, we can account for q-space components non-iteratively, using perturbation theory as follows. The vector of subspace cluster amplitudes, $\mathbf{t_p}$, defines $\bar{H}$, and we seek approximations to the energy and eigenvectors of $\bar{H}$, not just in the subspace $|\mathbf{p}\rangle$, but in the full space $|\mathbf{h}\rangle$. Due to the similarity transformation, there are distinct right and left eigenvectors, which we denote as $\hat{\mathbf{r}}|0\rangle$ and $\langle 0|\hat{\mathbf{l}}^{\dagger}$, with biorthogonal amplitudes $\mathbf{r}$ and $\mathbf{l}$ respec-

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tively. The transformed Schrödinger equation, $\bar{H}\hat{\mathbf{r}}|0\rangle = E\hat{\mathbf{r}}|0\rangle$ is projected with $\langle\mathbf{h}|$ to yield the matrix form, $\bar{\mathbf{H}}\mathbf{r} = E\mathbf{r}$. The energy itself is obtained by premultiplying by the adjoint of the left eigenvector amplitudes:

$$E = \mathbf{l}^\dagger\bar{\mathbf{H}}\mathbf{r}. \tag{3}$$

Splitting $\bar{\mathbf{H}} = \bar{\mathbf{H}}^{(0)} + \bar{\mathbf{H}}^{(1)}$, $\mathbf{r} = \mathbf{r}^{(0)} + \mathbf{r}^{(1)} + ...$, and $\mathbf{l} = \mathbf{l}^{(0)} + \mathbf{l}^{(1)} + ...$, and expanding eq. 3, we obtain corrections to the energy through second-order:

$$
\begin{aligned}
E^{(0)} &= \mathbf{l}^{\dagger(\mathbf{0})}\mathbf{H}^{(\mathbf{0})}\mathbf{r}^{(\mathbf{0})}, \\
E^{(1)} &= \mathbf{l}^{\dagger(\mathbf{0})}\mathbf{H}^{(\mathbf{1})}\mathbf{r}^{(\mathbf{0})}, \quad \text{and} \\
E^{(2)} &= \mathbf{l}^{\dagger(\mathbf{0})}\mathbf{H}^{(\mathbf{1})}\mathbf{r}^{(\mathbf{1})}.
\end{aligned}
\tag{4}
$$

We will choose $\mathbf{H}^{(\mathbf{0})} = \bar{\mathbf{H}}_{\mathbf{pp}} + \mathbf{F}_{\mathbf{qq}}$, $\mathbf{H}^{(\mathbf{1})} = \bar{\mathbf{H}}_{\mathbf{pq}} + \bar{\mathbf{H}}_{\mathbf{qp}} + \bar{\mathbf{V}}_{\mathbf{qq}} + \bar{\mathbf{F}}_{\mathbf{qq}} - \mathbf{F}_{\mathbf{qq}}$, $\mathbf{r}^{(0)} = \mathbf{1_p}$, and $\mathbf{l}^{(\mathbf{0})} = (\mathbf{1_p} + \mathbf{\Lambda_p})$, where Λ_p are the left-hand amplitudes from the coupled cluster pseudo-Lagrangian[104–106]. With these choices, we're guaranteed i) a zeroth-order eigenfunction of the transformed Hamiltonian equivalent to the $p-$space coupled cluster energy, $E^{(0)} = E^{\mathrm{CC}}$, ii) $E^{(1)} = 0$ since q- and p-space determinants cannot connect across the first-order Hamiltonian, and iii) uncoupled first-order amplitude equations following a basis transformation diagonalizing the energy difference.

Identifying the scope of $|\mathbf{p}\rangle$ determines the correlation model. Taking $|\mathbf{p}\rangle = |0\rangle + |\mathbf{s}\rangle + |\mathbf{d}\rangle$, $|\mathbf{h}\rangle = |\mathbf{t}\rangle + |\mathbf{q}\rangle$, and $\mathbf{H}_{\mathbf{qq}}^{(\mathbf{0})} = \bar{\mathbf{F}}_{\mathbf{qq}}$, for example, one obtains the "(2)" correction to CCSD[107] of Gwaltney *et. al.* A choice of bare $\mathbf{F}_{\mathbf{qq}}$ instead gives the "(2)$_{TQ}$"[108–110] corrections of Hirata. Neglecting quadruples, approximating $\mathbf{\Lambda} = \mathbf{t}^\dagger$, and retaining only binary contractions in the triples moment, one obtains CCSD(T). Though all are orbitally-invariant, a transformed one-body operator in the q space requires a fifth-order transformation to a set of biorthogonal eigenstates to diagonalize the amplitude equations. We therefore take the untransformed operator in the q space here.

After a change of basis and expansion of eq. 3, the equations for the first-order wavefunc-

tion are

$$\mathbf{D_{ss}^{(0)}} \mathbf{r_s^{(1)}} = \bar{\mathbf{H}}_{\mathbf{s0}}^{(1)} + \bar{\mathbf{H}}_{\mathbf{ss}}^{(1)} \mathbf{r_s^{(0)}} + \bar{\mathbf{H}}_{\mathbf{sd}}^{(1)} \mathbf{r_d^{(0)}} + \bar{\mathbf{H}}_{\mathbf{st}}^{(1)} \mathbf{r_t^{(0)}},$$

$$\mathbf{D_{dd}^{(0)}} \mathbf{r_d^{(1)}} = \bar{\mathbf{H}}_{\mathbf{d0}}^{(1)} + \bar{\mathbf{H}}_{\mathbf{ds}}^{(1)} \mathbf{r_s^{(0)}} + \bar{\mathbf{H}}_{\mathbf{dd}}^{(1)} \mathbf{r_d^{(0)}} + \bar{\mathbf{H}}_{\mathbf{dt}}^{(1)} \mathbf{r_t^{(0)}} + \bar{\mathbf{H}}_{\mathbf{dq}}^{(1)} \mathbf{r_q^{(0)}},$$

$$\mathbf{D_{tt}^{(0)}} \mathbf{r_t^{(1)}} = \bar{\mathbf{H}}_{\mathbf{t0}}^{(1)} + \bar{\mathbf{H}}_{\mathbf{ts}}^{(1)} \mathbf{r_s^{(0)}} + \bar{\mathbf{H}}_{\mathbf{td}}^{(1)} \mathbf{r_d^{(0)}} + \bar{\mathbf{H}}_{\mathbf{tt}}^{(1)} \mathbf{r_t^{(0)}} + \bar{\mathbf{H}}_{\mathbf{tq}}^{(1)} \mathbf{r_q^{(0)}}, \quad \text{and}$$

$$\mathbf{D_{qq}^{(0)}} \mathbf{r_q^{(1)}} = \bar{\mathbf{H}}_{\mathbf{q0}}^{(1)} + \bar{\mathbf{H}}_{\mathbf{qd}}^{(1)} \mathbf{r_d^{(0)}} + \bar{\mathbf{H}}_{\mathbf{qt}}^{(1)} \mathbf{r_t^{(0)}} + \bar{\mathbf{H}}_{\mathbf{qq}}^{(1)} \mathbf{r_q^{(0)}}. \tag{5}$$

where $\mathbf{D_{qq}^{(0)}} \equiv \{E^{(0)} \mathbf{1}_{qq} - \bar{\mathbf{H}}_{\mathbf{qq}}^{(0)}\}$. Applying these to the expression for the second-order energy above, we obtain

$$E^{(2)} = \bar{\mathbf{H}}_{\mathbf{0s}}^{(1)} \mathbf{r_s}^{(1)} + \bar{\mathbf{H}}_{\mathbf{0s}}^{(1)} \mathbf{r_d}^{(1)} +$$
$$\left(\mathbf{\Lambda_s}^{(0)} \right) \bar{\mathbf{H}}_{\mathbf{ss}}^{(1)} \mathbf{r_s}^{(1)} + \left(\mathbf{\Lambda_d}^{(0)} \right) \bar{\mathbf{H}}_{\mathbf{ds}}^{(1)} \mathbf{r_s}^{(1)} + \left(\mathbf{\Lambda_s}^{(0)} \right) \bar{\mathbf{H}}_{\mathbf{sd}}^{(1)} \mathbf{r_d}^{(1)} + \left(\mathbf{\Lambda_d}^{(0)} \right) \bar{\mathbf{H}}_{\mathbf{dd}}^{(1)} \mathbf{r_d}^{(1)} + \tag{6}$$
$$\left(\mathbf{\Lambda_s}^{(0)} \right) \bar{\mathbf{H}}_{\mathbf{st}}^{(1)} \mathbf{r_t}^{(1)} + \left(\mathbf{\Lambda_d}^{(0)} \right) \bar{\mathbf{H}}_{\mathbf{dt}}^{(1)} \mathbf{r_t}^{(1)} + \left(\mathbf{\Lambda_d}^{(0)} \right) \bar{\mathbf{H}}_{\mathbf{dq}}^{(1)} \mathbf{r_q}^{(1)}.$$

The generality of a similarity-transformed perturbation theory no doubt affords one a flexible framework within which various correlation models can be dreamt up and, as has been discussed, where others can be subsumed. It has proven itself a natural framework for extending active-space correlation to the external domains of orbital-optimized[111,112] and pair references[113,114], excited-state theories[115–118], and other formulations. Below, we couch a description of intermolecular interactions in a (2)-type model partitioning the configuration space to obtain molecule-centered coupled cluster states as zeroth-order wavefunctions.

B.   Nonorthogonal local correlation models for clusters using STPT

Beginning with a solution to the ALMO SCF problem, call it $|0\rangle$, we restrict the primary space to include $|0\rangle$ and the set of singly- and doubly-substituted determinants where excitations are *confined to one molecular site*,

$$|\mathbf{p}\rangle = |0\rangle + |\mathbf{s}_{\{ia\}}\rangle + |\mathbf{d}_{\{iajb\}}\rangle, \tag{7}$$

where the braces indicate that the associated indices are restricted such that all are associated with a single molecule (which we will also refer to as a "center"). Its complement includes two-center single excitations through four-center double excitations, as well as full-rank triples,

quadruples, etc., though in the present work we choose to restrict our attention to singles and doubles in order to benchmark non-locality errors against standard CCSD,

$$|\mathbf{q}\rangle = |\mathbf{s}_{\{i\}\{a\}}\rangle + |\mathbf{d}_{\{ia\}\{jb\}}\rangle + |\mathbf{d}_{\{i\}\{a\}\{jb\}}\rangle + ... + |\mathbf{d}_{\{i\}\{a\}\{j\}\{b\}}\rangle. \tag{8}$$

Applying this Hilbert-space partitioning and the same definitions as above for the Hamiltonian and the left and right zeroth-order states to eqs. 4, we obtain a coupled cluster-quality description of local excitations, and a non-iterative treatment of the interaction complete to fourth order in MP theory. Because the number of p-space variables scales linearly with the number of molecules, we refer to this theory henceforth as the "linear" model. Its instructive value notwithstanding, we shall expect to find this model wanting when higher-order correlations become significant.

Given free rein to specify $|\mathbf{p}\rangle$, one can imagine developing a hierarchy of schemes augmenting it to completeness in the space of singles and doubles, whereby the zeroth-order solution would be exact and there would be no perturbative correction to the energy and wavefunction. A first logical improvement to the linear reference would be to include a quadratic number of dispersion-type configurations explicitly coupling two bodies, but confining hole-particle excitations to emanate from either center, e.g., $\{|\mathbf{d}_{\{ia\}\{jb\}}\rangle\}$, in the reference space. Such an ansatz is reminiscent of the DIM-MP2 model for atom-centered local correlations[64,65], and an evaluation of the zeroth-order energy with first-order amplitudes should produce exactly that model. Promoting this class of excitations from a fourth- to an infinite-order treatment, we should expect to recover the bulk of the truncation error in dispersion interactions, where inductive and dative/charge-transfer-type effects are vanishing and repulsions dominate the mean-field interaction.

Further augmentation of the p space with a quadratic number of non-local singles (nls), e.g. $\{|\mathbf{s}_{\{i\}\{a\}}\rangle\}$, is expected to relax the local-orbital reference with respect to inter-site occupied-virtual rotations, recovering the bulk of the truncation error in cases where charge-transfer effects - which are omitted in the ALMO reference determinant - are substantial.

Still better, adding in the remaining non-local doubles defines a quartic model with the same number of variables as canonical CCSD, which is of course equivalent if $|0\rangle = |HF\rangle$. This model shall thus serve as a useful Hylleraas bound to assess the performance of our

model	$|\mathbf{d}\rangle$	$|\mathbf{s}\rangle$
linear	$\{iajb\}$	$\{ia\}$
linear+nls	$\{iajb\}$	$\{i\}\{a\}$
quadratic	$\{ia\}\{jb\}$	$\{i\}\{a\}$
quartic	$\{i\}\{a\}\{j\}\{b\}$	$\{i\}\{a\}$

TABLE I: Model specifics. Enclosed indices are restricted such that they are all associated or tagged to a single molecule (or "center"). Each model is named for its cost-scaling in the number of monomers.

upper-bound truncation models. We summarize their properties in Table I.

Since our models are defined in a Hilbert space of excitations from a non-orthogonal ALMO reference, we shall derive working equations for the p-space CC reference, and the q-space perturbation correction that make no assumption of spin-orbital orthogonality. We emphasize that the following equations are appropriate in any representation and reduce exactly to the conventional expressions with orthogonal orbitals diagonalizing the Fock matrix in the occupied and virtual sub-blocks. We begin in the biorthogonal[119,120] representation where given local occupied and virtual orbitals are covariant. Where they occur, repeated indices imply Einstein summation and contra- and covariant indices may be inter-converted by multiplication with the overlap g_{pq} or the inverse overlap g^{pq} metric, e.g., $C^{ij}_{ab} = g^{ik}g^{jl}C_{klab}$. Given any choice of $|\mathbf{p}\rangle$, the symmetric component of the zeroth-order energy and amplitude equations in the natural representation are

$$E^{(0)} = E^{\text{CCSD}} = f^i_a t^a_i + \frac{1}{4}v^{ij}_{ab}t^{ab}_{ij} + \frac{1}{2}v^{ij}_{ab}t^a_i t^b_j,$$

$$\langle^a_i|\bar{H}|0\rangle = f^a_b t^b_i - t^a_j f^j_i + A^a_i(t_1, t_2) = 0, \text{ and} \tag{9}$$

$$\langle^{ab}_{ij}|\bar{H}|0\rangle = f^a_c t^{cb}_{ij} + f^b_d t^{ad}_{ij} - t^{ab}_{kj}f^k_i - t^{ab}_{il}f^l_j + B^{ab}_{ij}(t_1, t_2) = 0.$$

In eqs.9, it is understood that the index pairs included in $\langle^a_i|$ and $\langle^{ab}_{ij}|$ are restricted according to the definition of $|\mathbf{p}\rangle$. Spin-orbital expressions for the second-rank tensor, A^a_i, and the fourth-rank tensor, B^{ab}_{ij}, in the *covariant* integral representation are given in Appendix A 1.

Applying the virtual-block metric to eliminate the left-hand inverses and the occupied metric to bring the amplitudes to contravariance, we recast the above equations in the co-

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variant integral representation and regroup terms obtaining,

$$E^{\text{CCSD}} = f_{ia}t^{ai} + \frac{1}{4}v_{ijab}t^{abij} + \frac{1}{2}v_{ijab}t^{ai}t^{bj},$$

$$\{f_{ji}g_{ab} - f_{ab}g_{ij}\}t^{bj} = A_{ai}(\bar{t}), \text{ and} \qquad (10)$$

$$\left\{ \{f_{lj}g_{bd} - f_{bd}g_{jl}\}g_{ki}g_{ac} + \{f_{ik}g_{ac} - f_{ac}g_{ik}\}g_{bd}g_{jl} \right\}t^{cdkl} = B_{abij}(\bar{t}).$$

With orthogonal orbitals, Kronecker deltas would replace the metrics and we'd need only pseudocanonicalize the orbitals to uncouple the amplitude equations. In a basis of non-canonical, non-orthogonal orbitals, our task will thus be to find a transformation that simultaneously orthogonalizes and pseudocanonicalizes the orbitals. Exploiting the direct-product structure of eq. 10, we define $G_{(ia)(jb)} = g_{ij}g_{ab}$ and $D_{(ia)(jb)} = \{f_{ij}g_{ab} - f_{ab}g_{ij}\}$ for convenience and rewrite the equations combining hole-particle pairs into compound indices "(ia)". This will be useful for thinking about pairwise truncations in our model spaces later on.

$$D_{(ia)(jb)}t^{(jb)} = A_{(ai)}(\bar{t}), \{D_{(bj)(ld)}G_{(ia)(kc)} + G_{(bj)(ld)}D_{(ia)(kc)}\}t^{(kc)(ld)} = B_{(ai)(jb)}(\bar{t}). \qquad (11)$$

Applying the transformation $T_{(AI)}^{(ai)} = G_{(jb)}^{-\frac{1}{2}(ai)}U_{(AI)}^{(jb)}$ where $U_{(AI)}^{(jb)}$ diagonalizes the energy-difference direct product, the amplitude equations assume a convenient diagonal form, $\underline{D}_p\bar{t}^p = \underline{R}_p$. Without making use of sparse linear algebra solvers, the diagonalization scales as $\mathcal{O}(P)^3$, where P is the number of correlated occupied-virtual pairs. The amplitudes must be back-transformed before updating the right-hand side, and special care must be taken to ensure all contractions in $\underline{R}_P$ respect the covariant integral representation, keeping the amplitudes contravariant. Moreover, consistent formulation of truncated flavors of eq. 11 requires that the two-particle direct product be formed in the same basis at the outset. For example, consider the quadratic model detailed above. There, the amplitude equations take a two-center metric composed strictly of overlaps spanning up to two fragments. The scope of the correlation problem is therefore fixed at the beginning by this designation.

The left-hand problem for $\hat{\Lambda}$ is isomorphic to the right-hand projection problem and, as such, must be consistently framed, e.g., if truncations were made in $\hat{T}$, the left-hand equations must also bear them out. We begin from the natural representation and again seek to recast these in the more convenient covariant matrix integral representation. Projecting the left-hand eigenvalue problem $\langle 0|\hat{L}\bar{H} = \langle 0|\hat{L}E$ onto the p-space singles and doubles, we obtain

the linear equations

$$X_a^i \equiv \langle 0|\bar{H}|_i^a\rangle + \lambda_b^j\langle_j^b|\bar{H}|_i^a\rangle + \lambda_{bc}^{jk}\langle_{jk}^{bc}|\bar{H}|_i^a\rangle = \lambda_a^i E, \text{ and}$$

$$Y_{ab}^{ij} \equiv \langle 0|\bar{H}|_{ij}^{ab}\rangle + \lambda_b^j\langle_j^b|\bar{H}|_{ij}^{ab}\rangle + \lambda_{bc}^{jk}\langle_{jk}^{bc}|\bar{H}|_{ij}^{ab}\rangle = \lambda_{ij}^{ab} E. \tag{12}$$

The spin-orbital equations for the matrix elements in the *covariant* representation are given in Appendix A 2. After subtracting the diagonal and applying the virtual block metric to take λ to the contravariant space and the occupied metric to make the left-hand side covariant, we obtain the similar form

$$X_{ia} = \lambda^{jb}\{f_{ji}g_{ab} - f_{ab}g_{ij}\}, \text{ and}$$

$$Y_{ijab} = \lambda^{klcd}\Big\{\{f_{lj}g_{bd} - f_{bd}g_{jl}\}g_{ki}g_{ac} + \{f_{ik}g_{ac} - f_{ac}g_{ik}\}g_{bd}g_{jl}\Big\}. \tag{13}$$

The same transformation as before diagonalizes the energy difference. Again, the covariant representation must be respected when updating the left-hand side and evaluating residuals.

By this point we have detailed the working equations sufficient to solve a non-orthogonal CCSD problem permitting truncations. Regarding our local cluster amplitudes as zeroth-order quantities, we proceed with a discussion of some features of the perturbation theory. As in the case of the zeroth-order amplitude equations, the scope of the perturbation will be fixed by the transformation applied to bring the first-order amplitude eqs.5 to diagonal form. Thus, a first-order amplitude describing an excitation across fragments, e.g., $\left[r^{(1)}\right]^{\{i\}\{jab\}}$, can only be consistently determined in a basis where the corresponding direct-product elements are taken into account, which means either the full-rank two-particle metric must be constructed and diagonalized as above, or one may equivalently solve for the first-order amplitudes in the biorthogonal representation. There, the amplitude equations are uncoupled after pseudo-canonicalization of the biorthogonal (non-Hermitian) Fock operator, at the risk of obtaining complex eigenvalues. Spin-orbital equations in the covariant integral representation for the first-order amplitudes and intermediates are given in Appendix A 3.

III. APPLICATIONS

All models were implemented in a modified version of Q-Chem[121,122] taking spin-orbital expressions for matrix elements of the transformed Hamiltonian generated by applying Wick's

theorem in an independent Mathematica code. The implementation relies on the tensor library recently developed[123] to facilitate Q-Chem's conventional coupled cluster capabilities. Scripts are available from your correspondents by request.

By our applications below, we aim to understand the extent to which non-local contributions will require an infinite-order treatment for prototypical interactions, or in other words, which components of the interaction are sufficiently small to be confidently relegated to a second-order STPT treatment. We take the truncated and quartic models to represent upper and lower bounds to the coupled cluster energy. The task of the perturbation theory is to bridge from one to the other. The success or failure of STPT in this task will be a measure of the physical appropriateness of the truncated CC reference.

A. Helium dimer

We have chosen the helium dimer interaction for initial studies. Given that the zeroth-order solution in any truncation scheme is exact at infinite separation for this case, we may cleanly ascribe any binding to the STPT at finite separation. Moreover, the purely dispersive nature of the interaction should, in the limit of a complete one-particle basis set, remove the effects of the orbital reference (any binding at the SCF level is an artifact of BSSE, while the constrained nature of the ALMO solution makes it an upper bound to full SCF), which is an important consideration when appraising candidate models against conventional CCSD. We plot He_2 potential curves furnished by STPT models with linear and quadratic doubles plus either linear or quadratic singles in Figure 1. It is evident that the difference in binding on the inclusion of non-local singles is relatively small for any truncation model, so we focus first on differences stemming from the level of treatment of the doubles. Examining the top two curves, it is clear that augmenting the on-site model with dispersion-type amplitudes binds the complex at zeroth-order, albeit shallowly and more distantly compared to the quartic model, which overlays canonical CCSD here. Treating all non-local doubles by the (2) correction to the linear model produces a bound state, but with a protracted, shallow minimum. On the other hand, an infinite-order description of dispersive doubles followed by a perturbative treatment of the rest propels the quadratic model to near-exactness, with any difference against the Hylleraas bound due to higher-than-fourth-order non-local effects in the doubles. We conclude that infinite-order dispersive doubles are critical to describe this interaction,

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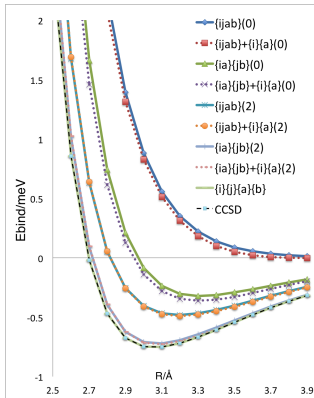
FIG. 1: He$_2$ potential curves in meV, computed in the aug-cc-pVTZ basis[124,125]. The local CCSD references (denoted "(0)") involve restricting some or all of the indices of the single and double substitution amplitudes to single centers to lower the complexity, as summarized in Table I. Indices enclosed in braces are restricted to a center: as in the case of the $\{ia\}$ singles.

while higher-order effects due to other non-local doubles are apparently negligible. Other tests shall be required to demonstrate the generality of these conclusions.

Returning to the non-local singles, it is no real surprise that they're uninteresting here, since the canonical and ALMO SCF solutions are rapidly approaching equivalence away from the repulsive wall. Nevertheless, we should expect in this incomplete basis that an infinite-order treatment of singles should recover more of the mean-field locality error than a perturbative treatment. To examine the difference, we compare the second-order contribution to eq. 6 due to linear singles against the infinite-order non-Brillouin term of eq. 10 garnered by quadratic singles, taking quadratic zeroth-order doubles in both cases. These are plotted alongside the ALMO error for the He$_2$ dimer in Figure 2, where it is confirmed that infinite-order singles recover more of the ALMO error than their perturbative cousins across the entire coordinate. We expect this difference to play a more significant role in cases where strong inter-fragment occupied-virtual interactions and/or inadequacies in the basis set produce a poor local reference. Indeed, glancing at Table II, we see the largest reduction in error due non-local singles in smaller, un-augmented basis sets. All errors have converged by the augmented quadruple-zeta level where non-local singles do not improve binding, and where including dispersion-type doubles in the p space results in a ten-fold reduction of error relative to a second-order treatment.

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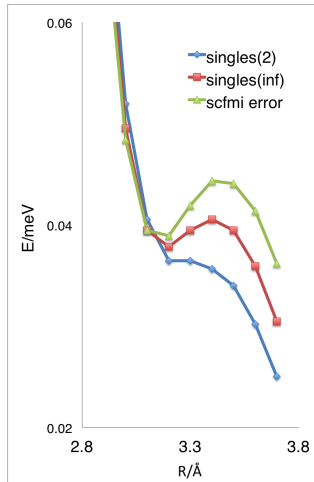
FIG. 2: Comparison of the magnitude of the energy recovered from perturbative (2) and infinite-order (inf) treatment of the non-local singles for He_2 in the aug-cc-pVTZ basis set relative to the magnitude of the error in the ALMO SCF calculation (SCFMI) versus unconstrained SCF. Perfect recovery would yield a singles curve identical with the ALMO error curve.

basis	$\{ijab\}^{(2)}$	$\{ijab\} + \{i\}\{a\}^{(2)}$	$\{ia\}\{jb\}^{(2)}$	$\{ia\}\{jb\} + \{i\}\{a\}^{(2)}$	$\{i\}\{j\}\{a\}\{b\}$	MP2	E_{CCSD}^{bind}
DZ	0.027	0.017	0.012	0.002	0.000	0.004	-0.131
TZ	0.071	0.057	0.019	0.005	0.000	0.017	-0.235
QZ	0.128	0.118	0.019	0.009	0.000	0.044	-0.315
aDZ	0.424	0.355	0.150	0.081	0.001	0.105	-1.081
aTZ	0.344	0.340	0.039	0.035	0.000	0.167	-0.749
aQZ	0.343	0.344	0.032	0.032	0.000	0.165	-0.763

TABLE II: CCSD/(aug-)cc-pVXZ interaction errors in meV relative to canonical CCSD for He_2 at its equilibrium internuclear separation. The "XZ" labels indicate the Dunning cc-pVXZ basis[124,125], while "aXZ" indicates the Dunning aug-cc-pVXZ[124,125].

How does a consideration of basis set superposition error affect our conclusions? By construction, our ALMO reference excludes BSSE, and all of our truncation models exclude from the p space determinants coupling inter-site occupied-virtual pairs (see Table I). BSSE must lurk in the non-local correction to the energy, then. To find out where, we computed BSSEs by the standard Boys-Bernardi counterpoise (CP) correction[126], compiling them alongside the change in the error in Table III. In all cases, CP correction results in an error reduction because intrinsic correlations are better represented. BSSE does not depend on the quality of the doubles, but does depend on the order at which the non-local singles are treated, with a non-zero contribution due to higher-order relaxation of t_1 even at the quadruple-zeta level. Taking the difference in BSSEs computed between any model with non-local singles and the quartic model will give the contribution to BSSE of higher-than-second-order non-

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basis	$\{ijab\}^{(2)}$	$\{ijab\} + \{i\}\{a\}^{(2)}$	$\{ia\}\{jb\}^{(2)}$	$\{ia\}\{jb\} + \{i\}\{a\}^{(2)}$	$\{i\}\{j\}\{a\}\{b\}$	HF+CCSD
aDZ	0.626 / -0.11	0.687 / -0.05	0.626 / -0.11	0.687 / -0.05	0.737 / 0.00	0.737 / -
aTZ	0.109 / -0.05	0.116 / -0.00	0.109 / -0.05	0.116 / -0.00	0.119 / 0.00	0.119 / -
aQZ	0.064 / 0.00	0.068 / -0.00	0.064 / 0.00	0.068 / -0.00	0.068 / 0.00	0.068 / -

TABLE III: BSSE correction (left)/change in binding error on counterpoise correction (right) for (2) corrections for the He_2 interaction at its equilibrium separation. "aXZ" indicates the Dunning aug-cc-pVXZ basis. BSSE and binding error changes both decrease as the basis set approaches completeness.

local doubles. These effects die more steeply with basis than non-local singles because their contributions are much smaller.

The fact that BSSE is nearly invariant to the reference is very interesting, and seems to have clear physical implications. We know from Table II that the perturbative correction to the linear doubles model, $\{iajb\}$, performs quite poorly relative to the quadratic doubles model, $\{ia\}\{jb\}$. Yet the BSSE error is recovered almost perfectly by the same approach. By this, we infer that the BSSE is *not* associated with the subclass of pair correlations which is treated poorly by the (2) correction to the linear model, and therefore must lie in the charge-transfer-type doubles.

B. Larger helium clusters

Do the conclusions we've drawn pertaining to the dimer also hold for small clusters of helium? Answering this question will inform us of the extent to which our local constructions can capture non-local effects coupling more than two bodies, which may seem daunting at first since, as the reader will recall, neither the linear nor quadratic model is able to couple more than two molecules explicitly at zeroth-order. We saw for the dimer that a Hilbert-space partitioning placing on-site and dispersion-type doubles in the p space and the rest in the q space proved adequate to recover the full-rank result, or in other words, that a second-order description of non-local doubles between two bodies sufficiently approximated the infinite-order description. There is no *apriori* guarantee that this should apply to larger interactions simply because the number of non-local doubles scales quartically with cluster size while the number of zeroth-order variables can only increase quadratically. Of course, one may argue on the basis of the intrinsic locality of dynamic correlations that the most important interactions in a cluster of weakly-interacting subsystems, though they may not be the most numerous,

	$\{ijab\}^{(2)}$	$\{ijab\}+\{i\}\{a\}^{(2)}$	$\{ia\}\{jb\}^{(2)}$	$\{ia\}\{jb\}+\{i\}\{a\}^{(2)}$	$\{i\}\{j\}\{a\}\{b\}$	MP2	E_{CCSD}^{bind}
$D_3/n=3$	0.93	0.93	0.11	0.10	0.00	0.46	-8.70
$T_d/n=4$	1.10	1.08	0.12	0.10	0.00	0.55	-11.60
$C_{4v}/n=5$	2.68	2.58	0.33	0.24	0.00	1.30	-14.50
$D_{5h}/n=7$	5.39	5.17	0.71	0.50	0.00	2.62	-20.30

TABLE IV: Binding errors (kJ/mol) for the second-order perturbation theory with various zeroth-order references (shown in the top row) relative to canonical CCSD/aug-cc-pVTZ. Higher-order dispersion is required. Structures are pictured in Fig. 4.

are two-body in nature, and therefore expect to have no issue relegating effects entangling more than two fragments to a perturbative treatment. If one adopts this optimistic outlook, one should expect the cluster problem to look like a collection of weakly-coupled dimeric ones, and thus expect the error to be most sensitive to two-body errors. Our local models, by construction, put us in good position to examine higher-order effects in clusters. As we have seen, the difference in performance between the linear and quadratic models reflects higher-order dispersion-like excitations coupling two bodies, while the difference between the quadratic and quartic models is a measure of the strength of higher-order inter-site couplings entangling up to four bodies. For the remainder of this discussion, well refer to these as higher-order local and non-local doubles. Taking an idealized linear cluster of helium atoms as our test application, we plot the dependence of higher-order contributions on cluster size in Fig. 3. In the limit of an infinite chain length, the one-dimensionality forces any two n-body interactions to be identical, and also guarantees the number of important n-body interactions to grow linearly, eliminating certain confounds in our benchmark. Examining the plot, we conclude that most of the higher-order contribution is in the local doubles, and moreover, that at least an infinite-order treatment there is indispensable.

We turn our attention to a set of more realistic clusters of helium, shown in Figure 4. Examining the models' binding errors relative to canonical CCSD in Table IV, we see in all cases, again, that the interaction error decreases roughly ten-fold on the inclusion of the quadratic dispersion amplitudes in the zeroth-order reference. The fact that a narrow 1-3% error bracket is achieved suggests again that higher-order non-local effects on binding are small. In particular, it is encouraging that the quadratic reference model yields errors roughly a factor of five smaller than MP2 theory, while it is interesting that the linear reference model yields errors roughly two-fold larger.
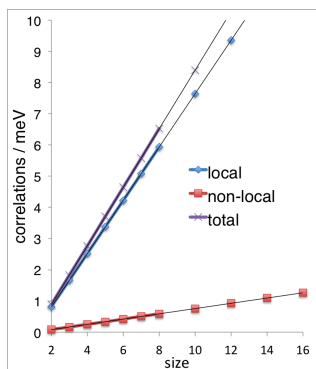
FIG. 3: Infinite-order local (two-body dispersion-type) and non-local (two- through four-body charge-transfer-type) doubles contributions to the correlation binding energy computed as a function of helium chain length. Local doubles are responsible for the bulk of binding effects. Calculations were performed in the aug-cc-pVDZ basis, and the geometries use a He-He spacing of 3.0Å.

$D_3 \, / \, _{n=3}$

$T_d \, / \, _{n=4}$

$C_{4v} \, / \, _{n=5}$

$D_{5h} \, / \, _{n=7}$
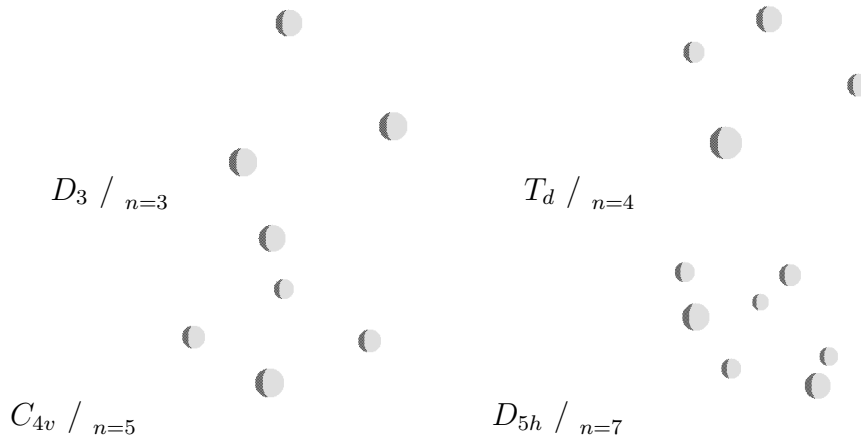
FIG. 4: He_n clusters. Geometries were optimized at the CCSD/aug-cc-pVTZ level.

C. Role of orbital non-orthogonality

Studies on clusters invite the important consideration of whether further tractability gains can be achieved by simplifying the implementation and costly operations required to diagonalize eq. 11 and compute matrix elements, all of which require contraction with explicit overlap metrics in both subspaces (see the Appendix). Up to this point, we have taken a reference determinant of fully non-orthogonal ALMOs. It shall be useful to consider the extent to which orthogonalization of either or both orbital subspaces will distort the domain definitions implied by the iSTPT and thereby degrade performance. Ideally, we'd prefer to orthogonalize both subspaces since then we'd only have to diagonalize the occupied and virtual blocks of the covariant Fock matrix to uncouple the amplitude equations and forgo

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dealing with any two-particle metric altogether, not to mention all one-body overlaps in the matrix elements reduce to Kronecker deltas. This approach is, of course, not expected to work, especially with the inclusion of more diffuse AO functions, a requirement for these applications. We return to the helium dimer interaction, computing the *change* in the interaction error going to orthogonal orbitals, compiling the data in the first rows of Table V. The insensitivity of the change in error to higher-order effects and a proportional increase with basis set extension reflects difficulty (and foolhardiness) in imputing orthogonalized orbitals to molecular centers, rendering a domain-definition framework ill-begotten. This is not to say that a localization technique will do nothing to improve the result insofar as symmetric orthogonalization will treat all functions on even footing, arguably producing the worst possible orthogonal functions. The second set of rows in Table V suggest the preliminary application of a localization scheme[127] furnishing atom-centered orthogonal virtuals and Boys-localized occupied orbitals does not help much.

One nevertheless has recourse in the argument that electing to orthogonalize the occupied space *alone* should not distort a given domain *too* much. This position is expected to be valid in the regime where inter-site overlaps are small (as is surely the case in helium clusters), and in cases where it minimally damages the locality, it will still effect speedup. The change in error starting from this "half-non-orthogonal" set of ALMOs is given in the final rows of Table V. Encouragingly, this procedure has no deleterious effects. Small "improvements" are likely the consequence of delocalization degrees of freedom the ALMOs enjoy on orthogonalization and should grow in proportion to charge-transfer and BSSE effects. We shall conduct more tests below to assess whether this result is the general case.

D. Inductive and dative interactions

We have yet to explore any interplay between local t_1 and the choice of orbital reference, e.g., whether there is a synergy or perhaps redundancy in optimizing t_1 beginning from a reference of ALMOs for which an intra-fragment Brillouin condition has been satisfied, e.g., induction has been treated to infinite-order. One can also imagine beginning from an un-optimized reference determinant of "frozen" orbitals - constructed from concatenating

orthogonalization	$\{ijab\}^{(2)}$	$\{ijab\} + \{i\}\{a\}^{(2)}$	$\{ia\}\{jb\}^{(2)}$	$\{ia\}\{jb\} + \{i\}\{a\}^{(2)}$
symmetric				
aDZ	1.79	1.82	1.80	1.83
aTZ	2.15	2.76	2.17	2.77
aQZ	3.20	4.10	3.23	4.13
symmetric, localized				
aDZ	1.78	1.81	1.79	1.82
aTZ	2.12	2.72	2.14	2.74
aQZ	3.15	4.04	3.18	4.06
half-non-orthogonal				
aDZ	-0.01	-0.01	-0.01	-0.01
aTZ	-0.01	-0.01	-0.01	-0.01
aQZ	0.00	-0.01	0.00	-0.01

TABLE V: Change in He_2 equilibrium interaction error on orthogonalization. Energies are in meV. Orthogonalization of both subspaces destroys domain identification, whereas orthogonalization of the occupied subspace alone preserves accuracy while conferring cost-savings. "aXZ" indicates the Dunning aug-cc-pVXZ basis.

fragment-blocked coefficient matrices determined as the SCF solutions of molecules in vacuum - and relying on the projective optimization of t_1 to polarize the orbitals. Surely the leading occupied-virtual Fock elements, which unambiguously account for mean-field polarization, will play a significant role in the optimization, but the extent to which the simultaneous optimization of correlations will influence the mean-field induction and *vice versa* is, at this point, unclear. The other question is whether neglecting t_1 altogether is compensated by choosing an ALMO starting point, in which case there can be no t_1-mediated mutual interaction of induction and correlation at zeroth-order.

We shall have to be careful when addressing these questions to choose a test system for which the ALMO solution is a good approximation to Hartree-Fock, e.g., where attractions attributed to dative effects are negligible and polarizations dominate mean-field binding. To this end we have chosen the interaction of helium with lithium cation. We conclude glancing at the first column of Table VI that repulsions destabilize the "frozen" wavefunction (FRZ) but are overridden by inductive effects described nearly perfectly going to the ALMOs, leaving a small "delocalization" error relative to canonical HF of 0.3 kJ/mol. Beginning from a frozen reference, we shift the onus onto intramonomer t_1 to recover mean-field polarization.

We apply our local models to the interaction beginning from both references, with and

SCF model	HeLi$^+$	NH$_3$BH$_3$
FRZ	1.24	105.20
ALMO	-5.35	-44.30
HF	-5.65	-146.54

TABLE VI: aug-cc-pVDZ Mean-field interaction energies for a predominantly inductive interaction (HeLi$^+$) and a predominantly dative interaction (NH$_3$BH$_3$) in kJ/mol. The geometries were optimized at the CCSD/aug-cc-pVDZ level. The ALMO orbitals are quantitative for the principally-inductive HeLi$^+$ interaction, but largely inadequate to describe the charge-transfer-dominated NH$_3$BH$_3$ interaction.

wavefunction	CCD		CCSD		CCSD
truncation model	$\{iajb\}$	$\{ia\}\{jb\}$	$\{iajb\}$	$\{ia\}\{jb\}$	$\{i\}\{a\}\{j\}\{b\}$
HeLi$^+$(FRZ)	2.25	2.24	0.09	0.08	0.00
HeLi$^+$(FRZ)+{i}{a}	-	-	0.05	0.04	-
HeLi$^+$(ALMO)	0.10	0.09	0.09	0.08	0.00
HeLi$^+$(ALMO)+{i}{a}	-	-	0.05	0.04	-
NH$_3$BH$_3$(FRZ)	112.26	102.08	63.17	53.72	14.12
NH$_3$BH$_3$(FRZ)+{i}{a}	-	-	31.26	23.38	-
NH$_3$BH$_3$(ALMO)	50.71	46.83	51.06	44.94	9.62
NH$_3$BH$_3$(ALMO)+{i}{a}	-	-	23.19	17.96	-

TABLE VII: Errors (in kJ/mol) relative to the canonical CCSD equilibrium binding energy computed in aug-cc-pVDZ taking various zeroth-order models. "$\{i\}\{a\}$" indicate the inclusion of non-local zeroth-order singles amplitudes. CCSD indicates that intramolecular singles are included at zero order, while they are excluded in CCD. $E_{\text{bind}}^{\text{CCSD}}$ (NH$_3$BH$_3$)= 177.07 kJ/mol. $E_{\text{bind}}^{\text{CCSD}}$(HeLi$^+$)= 6.65 kJ/mol. Intramolecular t_1 emulates the effects of ALMO optimization. Accounting for higher-order effects due to intermolecular t_1 is required to describe dative interactions.

without explicit singles in the correlation model. Interaction errors relative to canonical CCSD are given in the first rows of Table VII. In stark contrast to the helium results, there is virtually no dependence of the error on higher-order doubles. Moreover, it one arrives at the same error opting either to begin from ALMOs and neglecting singles altogether, or beginning from frozen orbitals and optimizing intramonomer t_1. Including non-local singles in the reference, we recover most of the remaining error, concluding, in line with our intuition, that infinite-order one-body effects trump infinite-order dispersion-type doubles in this case.

Another important question to consider is the extent to which the perturbation theory is viable when the ALMO reference is poor, such as when dative effects become important. Here, larger-magnitude intermolecular f$_{ov}$ elements and smaller band gaps no doubt elevate

intermolecular occupied-virtual rotations to such a significance that the ALMO error is no longer small. The reader will recall that for iSTPTs taking only on-site singles at zeroth-order, charge-transfer effects first enter at second order, so a description of dative interactions will likely suffer. We have chosen the C_{3v}-symmetry ammonia-borane dative interaction to measure the extent. It represents a particularly challenging case for a frozen-orbital reference (see the second column of Table VI), unstable by a walloping two-thirds of its canonical binding energy. ALMO relaxation adds some 150kJ/mol to the interaction, but it's still missing some 100kJ/mol of delocalization. Thus, a perturbative treatment beginning with either local reference will have a lot to clean up.

Examining the second set of rows of Table VII, one can see that augmenting the local models with (on-site) singles (i.e. compare the CCD vs CCSD entries) drastically improves the frozen-orbital models while scarcely affecting the relaxed-reference results. There is a similar improvement going from unrelaxed to relaxed orbitals neglecting local singles. Adding non-local singles to CCSD on top of either a frozen or relaxed orbital reference reduces the error against the quartic model most considerably, with the improvement relatively insensitive to truncation model. In view of these applications, we anticipate that the inclusion of non-local singles at zeroth-order will effect substantial accuracy gains when applied to cases where the local reference is wanting.

E.   Tests on the A24 dataset

Until now, we have focused on exposing properties of our local theories by applying them to model interactions. It remains to be seen how general our conclusions are. To this end, we apply our standard models and half-non-orthogonal variants thereof to the A24 dataset of non-covalent interactions which includes a varied set of hydrogen-bonded (HB), mixed-character (MIX), and dispersion-dominated (DISP) interactions[103]. Root-mean-square errors (RMSE) measured against canonical CCSD are given in Table VIII. Refer to Table IX in Appendix B for individual quantities. Calculations were performed in aug-cc-pVDZ using the frozen core approximation.

Unsurprisingly, the quartic model furnishes energetics virtually identical to CCSD across all interactions, so we can safely eliminate orbital-reference effects as a source of error. Thus, truncation model errors are almost entirely due to the Hilbert space partitioning. Including

	$\{ijab\}^{(2)}$	$\{ijab\}+\{i\}\{a\}^{(2)}$	$\{ijab\}+\{i\}\{a\}^{(2)}_{hno}$	$\{ia\}\{jb\}^{(2)}$	$\{ia\}\{jb\}+\{i\}\{a\}^{(2)}$	$\{ia\}\{jb\}+\{i\}\{a\}^{(2)}_{hno}$	$\{i\}\{j\}\{a\}\{b\}$	MP2
total	2.47	1.59	1.47	1.93	1.00	0.92 (0.65)	0.21	1.51 (1.32)
HB	3.68	1.88	1.63	3.01	1.21	1.05 (0.73)	0.21	1.38 (1.19)
MIX	2.51	1.76	1.59	1.93	1.09	0.96 (0.68)	0.25	1.38 (1.20)
DISP	1.09	1.13	1.09	0.67	0.71	0.67 (0.55)	0.17	1.72 (1.52)

TABLE VIII: A24 statistical errors in kJ/mol relative to CCSD. All calculations were performed in the aug-cc-pVDZ basis. The "hno" (half non-orthogonal) subscript means the occupied orbitals alone were symmetrically orthogonalized. Parenthetical numbers represent counterpoise-corrected quantities. Models taking quadratic singles and doubles at zeroth-order are nearly quantitative.

all singles in the p space substantially improves the RMSE for any doubles model, weighing most heavily on hydrogen-bonded and mixed interactions, but minimally affecting dispersion, as our test cases showed. Quadratic p-space doubles, on the other hand, yield significant improvements in the RMS errors for all classes of interactions. To beat MP2, these data suggest quadratic singles and doubles at zeroth-order are required in the HB and MIX categories, though any truncation model wins out for dispersion, suggesting steep improvement beyond a first-order MP treatment there. Our most promising truncation model incorporates quadratic singles and doubles at zeroth-order, and is superior to MP2 for all interaction types. The margin is more than a factor of two for the dispersion interactions. Similar conclusions are drawn for the half-non-orthogonal models, which again show uniform improvement relative to the fully-non-orthogonal models. While our pilot code confines us to smaller basis sets, we believe that improvements in our (2) results over MP2 in larger basis sets may be even more dramatic, because, based on our helium results in Table III, intrinsic correlations are better captured there. Indeed, counterpoise correction (given in parentheses) results in RMS error reductions much larger for the half-non-orthogonal model than for MP2.

IV. CONCLUSIONS

We have developed and applied a hierarchy of fully-non-orthogonal coupled cluster correlation models treating intermolecular interactions at second-order in similarity transformed (Löwdin) perturbation theory. Having cataloged the importance of various higher-order contributions in a host of applications, we have determined that infinite-order non-local singles are indispensable for dative interactions, while quadratic doubles are required for dispersion, and, indeed, most other intermolecular interactions. Benchmark computations indicate

our quadratic models nearly quantitatively approximate canonical CCSD, and further cost-reduction is achieved without a loss of accuracy by orthogonalizing the occupied subspace.

Future directions include characterization of fully-non-iterative models substituting first-order amplitudes for CCSD ones, and orbital optimization in the field of correlation to remove the singles amplitudes, as well as analysis of n-body effects in clusters and extension of the q space to include triple and quadruple excitations. In the regime where a perturbative treatment is valid, ALMO-based iSTPT models taking only a linear or quadratic number of zeroth-order CC variables represent natural routes to local coupled cluster theory.

V. ACKNOWLEDGMENTS

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Appendix A: Spin-orbital expressions in the covariant integral representation

Occupied and virtual orbitals are indexed $(i, j, k, l, I, J, K, L...)$ and $(a, b, c, d, A, B, C, D...)$, respectively, with upper-case indices implying external hole/particle excitations and lower-case (internal) indices implying summation. The operator a_{pq} is an antisymmetrizer, e.g., $a_{\mathrm{pq}} X_{pqrs} = X_{pqrs} - X_{qprs}$. The tensors f_{pq} and v_{pqrs} are the Fock and antisymmerized integrals, respectively. t, λ, r are the cluster, left, and first-order right amplitudes. The following intermediates are used in the expressions below.

$$X_h^{\mathrm{aI}} = X^{\mathrm{aj}} g_{\mathrm{jI}} \tag{A1}$$

$$X_p^{\mathrm{Ai}} = g_{\mathrm{Ab}} X^{\mathrm{bi}} \tag{A2}$$

$$X_h^{\mathrm{abIJ}} = g_{\mathrm{Ij}} X^{\mathrm{abjJ}} \tag{A3}$$

$$X_{pp}^{\mathrm{ABij}} = g_{\mathrm{Aa}} g_{\mathrm{Bb}} X^{\mathrm{abij}} \tag{A4}$$

$$X_{hp}^{\mathrm{bBiI}} = g_{\mathrm{ij}} g_{\mathrm{bc}} X^{\mathrm{cBjI}} \tag{A5}$$

$$X_{hp'}^{\mathrm{bBiI}} = g_{\mathrm{Ij}} g_{\mathrm{Bc}} X^{\mathrm{bcij}} \tag{A6}$$

$$X_{hph}^{\mathrm{bcij}} = g_{\mathrm{jk}} X_{hp}^{\mathrm{bcik}} \tag{A7}$$

$$X_{hpp}^{\mathrm{bcij}} = g_{\mathrm{ca}} X_{hp}^{\mathrm{baij}} \tag{A8}$$

1. CCSD amplitude equations

$$A_{AI}(\bar{t}) =$$

$$f_{\mathrm{AI}} \tag{A9}$$

$$f_{\mathrm{ai}} t_{hp}^{\mathrm{aAiI}} \tag{A10}$$

$$-1.f_{\mathrm{ai}} t_h^{\mathrm{aI}} t_p^{\mathrm{Ai}} \tag{A11}$$

$$-0.5 g_{\mathrm{aA}} v_{\mathrm{biIj}} t^{\mathrm{abij}} \tag{A12}$$

$$-0.5 g_{\mathrm{Ij}} v_{\mathrm{aAbi}} t^{\mathrm{abij}} \tag{A13}$$

$$-1.t^{\mathrm{ai}} v_{\mathrm{aAiI}} \tag{A14}$$

$$-1.t^{\mathrm{aj}} v_{\mathrm{aiIj}} t_p^{\mathrm{Ai}} \tag{A15}$$

$$-0.5 g_{\mathrm{aA}} v_{\mathrm{bcij}} t^{\mathrm{acij}} t_h^{\mathrm{bI}} \tag{A16}$$

$$t^{\mathrm{ai}} v_{\mathrm{abij}} t_{hp}^{\mathrm{AbIj}} \tag{A17}$$

$$-0.5 g_{\mathrm{Ik}} v_{\mathrm{abij}} t^{\mathrm{abjk}} t_p^{\mathrm{Ai}} \tag{A18}$$

$$-1.t^{\mathrm{bi}} v_{\mathrm{aAbi}} t_h^{\mathrm{aI}} \tag{A19}$$

$$-1.t^{\mathrm{bj}} v_{\mathrm{abij}} t_h^{\mathrm{aI}} t_p^{\mathrm{Ai}} \tag{A20}$$

$$B_{IJ}^{AB}(\bar{t}) =$$

$$-1.g_{\mathrm{aB}} a_{\mathrm{IJ}} f_{\mathrm{bi}} t_h^{\mathrm{bJ}} t_{hp}^{\mathrm{aAiI}} \tag{A21}$$

$$-1.f_{\mathrm{ai}} a_{\mathrm{AB}} g_{\mathrm{jJ}} t_p^{\mathrm{Bi}} t_{hp}^{\mathrm{aAIj}} \tag{A22}$$

$$v_{\mathrm{ABIJ}} \tag{A23}$$

$$0.5 v_{\mathrm{iIjJ}} t_{pp}^{\mathrm{ABij}} \tag{A24}$$

$$-1.a_{\mathrm{AB}} a_{\mathrm{IJ}} v_{\mathrm{aAiI}} t_{hp}^{\mathrm{aBiJ}} \tag{A25}$$

$$0.5 v_{\mathrm{aAbB}} t_h^{\mathrm{abIJ}} \tag{A26}$$

$$a_{\mathrm{AB}} v_{\mathrm{AiIJ}} t_p^{\mathrm{Bi}} \tag{A27}$$

$$a_{\mathrm{IJ}} v_{\mathrm{aABI}} t_h^{\mathrm{aJ}} \tag{A28}$$

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$$-1.a_{\text{AB}}v_{\text{abij}}t_{hp}^{\text{aBiI}}t_{hp}^{\text{AbjJ}} \tag{A29}$$

$$0.25v_{\text{abij}}t_{h}^{\text{abIJ}}t_{pp}^{\text{ABij}} \tag{A30}$$

$$-0.5g_{\text{aB}}g_{\text{Jk}}v_{\text{bcij}}t^{\text{bcjk}}t_{hp}^{\text{aAiI}} \tag{A31}$$

$$-0.5g_{\text{aB}}a_{\text{AB}}g_{\text{Jk}}v_{\text{bcij}}t^{\text{acij}}t_{hp}^{\text{AbIk}} \tag{A32}$$

$$-0.5g_{\text{aB}}g_{\text{Ik}}v_{\text{bcij}}t^{\text{bcik}}t_{hp}^{\text{aAjJ}} \tag{A33}$$

$$v_{\text{iIjJ}}t_{p}^{\text{Ai}}t_{p}^{\text{Bj}} \tag{A34}$$

$$a_{\text{AB}}a_{\text{IJ}}v_{\text{aiIj}}t_{p}^{\text{Bi}}t_{hp}^{\text{aAjJ}} \tag{A35}$$

$$0.5a_{\text{IJ}}v_{\text{aiIj}}t_{h}^{\text{aJ}}t_{pp}^{\text{ABij}} \tag{A36}$$

$$-1.g_{\text{aB}}a_{\text{IJ}}t^{\text{bi}}v_{\text{biIj}}t_{hp}^{\text{aAjJ}} \tag{A37}$$

$$a_{\text{AB}}a_{\text{IJ}}v_{\text{aAiI}}t_{h}^{\text{aJ}}t_{p}^{\text{Bi}} \tag{A38}$$

$$0.5a_{\text{AB}}v_{\text{aAbi}}t_{p}^{\text{Bi}}t_{h}^{\text{abIJ}} \tag{A39}$$

$$a_{\text{AB}}a_{\text{IJ}}v_{\text{aAbi}}t_{h}^{\text{aJ}}t_{hp}^{\text{bBiI}} \tag{A40}$$

$$-1.a_{\text{AB}}g_{\text{jJ}}t^{\text{ai}}v_{\text{aAbi}}t_{hp}^{\text{bBIj}} \tag{A41}$$

$$v_{\text{aAbB}}t_{h}^{\text{aI}}t_{h}^{\text{bJ}} \tag{A42}$$

$$a_{\text{IJ}}v_{\text{aiIj}}t_{h}^{\text{aJ}}t_{p}^{\text{Ai}}t_{p}^{\text{Bj}} \tag{A43}$$

$$0.5v_{\text{abij}}t_{p}^{\text{Ai}}t_{p}^{\text{Bj}}t_{h}^{\text{abIJ}} \tag{A44}$$

$$-1.a_{\text{AB}}a_{\text{IJ}}v_{\text{abij}}t_{h}^{\text{aJ}}t_{p}^{\text{Bi}}t_{hp}^{\text{AbIj}} \tag{A45}$$

$$-1.a_{\text{AB}}g_{\text{Jk}}t^{\text{ai}}v_{\text{abij}}t_{p}^{\text{Bj}}t_{hp}^{\text{AbIk}} \tag{A46}$$

$$0.5v_{\text{abij}}t_{h}^{\text{aI}}t_{h}^{\text{bJ}}t_{pp}^{\text{ABij}} \tag{A47}$$

$$g_{\text{aB}}a_{\text{IJ}}t^{\text{ci}}v_{\text{bcij}}t_{h}^{\text{bJ}}t_{hp}^{\text{aAIj}} \tag{A48}$$

$$a_{\text{AB}}v_{\text{aAbi}}t_{h}^{\text{aI}}t_{h}^{\text{bJ}}t_{p}^{\text{Bi}} \tag{A49}$$

$$v_{\text{abij}}t_{h}^{\text{aI}}t_{p}^{\text{Ai}}t_{h}^{\text{bJ}}t_{p}^{\text{Bj}} \tag{A50}$$

2. Left-hand singles and doubles equations

$$\lambda_b^j \langle_j^b | \bar{H} |_I^A \rangle =$$

$$f_{\mathrm{aA}} \lambda_h^{\mathrm{aI}} \tag{A51}$$

$$-1. f_{\mathrm{iI}} \lambda_p^{\mathrm{Ai}} \tag{A52}$$

$$-1. f_{\mathrm{Ai}} \lambda_h^{\mathrm{aI}} t_p^{\mathrm{ai}} \tag{A53}$$

$$-1. f_{\mathrm{aI}} t_h^{\mathrm{ai}} \lambda_p^{\mathrm{Ai}} \tag{A54}$$

$$-1. r^{\mathrm{ai}} v_{\mathrm{aAiI}} \tag{A55}$$

$$-0.5 g_{\mathrm{ab}} v_{\mathrm{Acij}} t^{\mathrm{acij}} \lambda_h^{\mathrm{bI}} \tag{A56}$$

$$r^{\mathrm{ai}} v_{\mathrm{AbIj}} t_{hp}^{\mathrm{abij}} \tag{A57}$$

$$-0.5 g_{\mathrm{Ab}} v_{\mathrm{aciI}} t^{\mathrm{acij}} \lambda_h^{\mathrm{bj}} \tag{A58}$$

$$r^{\mathrm{ai}} v_{\mathrm{AiIj}} t_p^{\mathrm{aj}} \tag{A59}$$

$$-1. t^{\mathrm{aj}} v_{\mathrm{aiIj}} \lambda_p^{\mathrm{Ai}} \tag{A60}$$

$$-1. t^{\mathrm{bi}} v_{\mathrm{aAbi}} \lambda_h^{\mathrm{aI}} \tag{A61}$$

$$r^{\mathrm{ai}} v_{\mathrm{aAbI}} t_h^{\mathrm{bi}} \tag{A62}$$

$$-1. t^{\mathrm{bj}} v_{\mathrm{Abij}} \lambda_h^{\mathrm{aI}} t_p^{\mathrm{ai}} \tag{A63}$$

$$-1. r^{\mathrm{ai}} v_{\mathrm{AbIj}} t_p^{\mathrm{aj}} t_h^{\mathrm{bi}} \tag{A64}$$

$$-1. t^{\mathrm{bj}} v_{\mathrm{abIj}} t_h^{\mathrm{ai}} \lambda_p^{\mathrm{Ai}} \tag{A65}$$

$$\lambda^{jk}_{bc}\langle^{bc}_{jk}|\bar{H}|^A_I\rangle =$$

$$1.f_{\mathrm{ai}}\lambda^{\mathrm{aAiI}}_{hp} \tag{A66}$$

$$1.f_{\mathrm{bj}}\lambda^{\mathrm{aAiI}}_{hp}t^{\mathrm{abij}}_{hp} \tag{A67}$$

$$0.5f_{\mathrm{Aj}}g_{\mathrm{bc}}g_{\mathrm{ik}}t^{\mathrm{acjk}}\lambda^{\mathrm{abiI}}_{hp} \tag{A68}$$

$$0.5g_{\mathrm{ab}}f_{\mathrm{cI}}g_{\mathrm{jk}}t^{\mathrm{acij}}\lambda^{\mathrm{Abik}}_{hp} \tag{A69}$$

$$-1.f_{\mathrm{ij}}t^{\mathrm{aj}}_{p}\lambda^{\mathrm{aAiI}}_{hp} \tag{A70}$$

$$1.f_{\mathrm{ab}}t^{\mathrm{bi}}_{h}\lambda^{\mathrm{aAiI}}_{hp} \tag{A71}$$

$$-1.f_{\mathrm{bj}}t^{\mathrm{aj}}_{p}t^{\mathrm{bi}}_{h}\lambda^{\mathrm{aAiI}}_{hp} \tag{A72}$$

$$-0.5g_{\mathrm{Ab}}v_{\mathrm{aiIj}}r^{\mathrm{abij}} \tag{A73}$$

$$-0.5g_{\mathrm{iI}}v_{\mathrm{aAbj}}r^{\mathrm{abij}} \tag{A74}$$

$$-0.25g_{\mathrm{bc}}v_{\mathrm{Aijk}}t^{\mathrm{acjk}}\lambda^{\mathrm{abiI}}_{hp} \tag{A75}$$

$$-0.25g_{\mathrm{ab}}v_{\mathrm{AiIj}}t^{\mathrm{acjk}}\lambda^{\mathrm{bcik}}_{hp'} \tag{A76}$$

$$-0.5g_{\mathrm{ab}}v_{\mathrm{cijk}}t^{\mathrm{acjk}}\lambda^{\mathrm{AbiI}}_{hp} \tag{A77}$$

$$-0.5g_{\mathrm{Ab}}v_{\mathrm{ciIj}}t^{\mathrm{acjk}}\lambda^{\mathrm{abik}}_{hp'} \tag{A78}$$

$$0.25g_{\mathrm{bc}}v_{\mathrm{AiIk}}t^{\mathrm{acij}}\lambda^{\mathrm{abjk}}_{hp} \tag{A79}$$

$$0.5g_{\mathrm{ab}}v_{\mathrm{ciIk}}t^{\mathrm{acij}}\lambda^{\mathrm{Abjk}}_{hp} \tag{A80}$$

$$0.5g_{\mathrm{ik}}v_{\mathrm{Abcj}}t^{\mathrm{acjk}}\lambda^{\mathrm{abiI}}_{hp} \tag{A81}$$

$$-0.5g_{\mathrm{iI}}v_{\mathrm{aAcj}}t^{\mathrm{bcjk}}\lambda^{\mathrm{abik}}_{hp'} \tag{A82}$$

$$0.25g_{\mathrm{jk}}v_{\mathrm{AbcI}}t^{\mathrm{acij}}\lambda^{\mathrm{abik}}_{hp} \tag{A83}$$

$$-0.25g_{\mathrm{ij}}v_{\mathrm{aAcI}}t^{\mathrm{bcjk}}\lambda^{\mathrm{abik}}_{hp'} \tag{A84}$$

$$-0.5g_{\mathrm{ik}}v_{\mathrm{abcj}}t^{\mathrm{bcjk}}\lambda^{\mathrm{aAiI}}_{hp} \tag{A85}$$

$$-0.25g_{\mathrm{jk}}v_{\mathrm{abcI}}t^{\mathrm{bcij}}\lambda^{\mathrm{aAik}}_{hp} \tag{A86}$$

$$0.5 g_{\mathrm{aA}} v_{\mathrm{iIjk}} r^{\mathrm{abik}} t_p^{\mathrm{bj}} \tag{A87}$$

$$0.5 t^{\mathrm{aj}} v_{\mathrm{Abij}} \lambda_{hp}^{\mathrm{abiI}} \tag{A88}$$

$$-0.5 g_{\mathrm{iI}} v_{\mathrm{aAjk}} r^{\mathrm{abij}} t_p^{\mathrm{bk}} \tag{A89}$$

$$-1. t^{\mathrm{bj}} v_{\mathrm{abij}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A90}$$

$$-0.5 g_{\mathrm{Ab}} v_{\mathrm{aciI}} r^{\mathrm{abij}} t_h^{\mathrm{cj}} \tag{A91}$$

$$0.5 t^{\mathrm{bi}} v_{\mathrm{abIj}} \lambda_{hp}^{\mathrm{aAij}} \tag{A92}$$

$$0.5 g_{\mathrm{iI}} v_{\mathrm{aAbc}} r^{\mathrm{abij}} t_h^{\mathrm{cj}} \tag{A93}$$

$$-0.5 t^{\mathrm{aj}} v_{\mathrm{Aijk}} t_p^{\mathrm{bk}} \lambda_{hp}^{\mathrm{abiI}} \tag{A94}$$

$$-1. t^{\mathrm{bk}} v_{\mathrm{bijk}} t_p^{\mathrm{aj}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A95}$$

$$0.5 g_{\mathrm{Ab}} t^{\mathrm{aj}} t^{\mathrm{ck}} v_{\mathrm{ciIj}} \lambda_{hp'}^{\mathrm{abik}} \tag{A96}$$

$$-0.5 t^{\mathrm{bj}} v_{\mathrm{biIk}} t_p^{\mathrm{ai}} \lambda_{hp}^{\mathrm{aAjk}} \tag{A97}$$

$$0.25 g_{\mathrm{bc}} v_{\mathrm{Adjk}} t^{\mathrm{acjk}} t_h^{\mathrm{di}} \lambda_{hp}^{\mathrm{abiI}} \tag{A98}$$

$$-0.5 g_{\mathrm{bc}} g_{\mathrm{il}} t^{\mathrm{dj}} v_{\mathrm{Adjk}} t^{\mathrm{ackl}} \lambda_{hp}^{\mathrm{abiI}} \tag{A99}$$

$$-0.25 g_{\mathrm{bc}} v_{\mathrm{AdiI}} t^{\mathrm{acij}} t_h^{\mathrm{dk}} \lambda_{hp}^{\mathrm{abjk}} \tag{A100}$$

$$0.25 g_{\mathrm{bc}} g_{\mathrm{kl}} t^{\mathrm{dj}} v_{\mathrm{AdiI}} t^{\mathrm{acik}} \lambda_{hp}^{\mathrm{abjl}} \tag{A101}$$

$$0.5 g_{\mathrm{il}} v_{\mathrm{Acjk}} t^{\mathrm{ackl}} t_p^{\mathrm{bj}} \lambda_{hp}^{\mathrm{abiI}} \tag{A102}$$

$$-0.5 t^{\mathrm{aj}} v_{\mathrm{Acjk}} \lambda_{hp}^{\mathrm{abiI}} t_{hp}^{\mathrm{bcik}} \tag{A103}$$

$$-0.25 g_{\mathrm{kl}} v_{\mathrm{AciI}} t^{\mathrm{acjk}} t_p^{\mathrm{bi}} \lambda_{hp}^{\mathrm{abjl}} \tag{A104}$$

$$0.25 g_{\mathrm{bc}} g_{\mathrm{kl}} t^{\mathrm{ai}} v_{\mathrm{AdiI}} t^{\mathrm{cdjk}} \lambda_{hp}^{\mathrm{abjl}} \tag{A105}$$

$$-0.5 g_{\mathrm{ab}} v_{\mathrm{cdjk}} t^{\mathrm{adjk}} t_h^{\mathrm{ci}} \lambda_{hp}^{\mathrm{AbiI}} \tag{A106}$$

$$1. t^{\mathrm{bj}} v_{\mathrm{bcjk}} \lambda_{hp}^{\mathrm{aAiI}} t_{hp}^{\mathrm{acik}} \tag{A107}$$

$$0.5 g_{\mathrm{ab}} v_{\mathrm{cdiI}} t^{\mathrm{adij}} t_h^{\mathrm{ck}} \lambda_{hp}^{\mathrm{Abjk}} \tag{A108}$$

$$-0.5 t^{\mathrm{bj}} v_{\mathrm{bciI}} \lambda_{hp}^{\mathrm{aAjk}} t_{hp}^{\mathrm{acik}} \tag{A109}$$

$$-0.5 g_{\mathrm{il}} v_{\mathrm{bcjk}} t_p^{\mathrm{aj}} t^{\mathrm{bckl}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A110}$$

$$-0.5 g_{\mathrm{ab}} g_{\mathrm{kl}} t^{\mathrm{ci}} v_{\mathrm{cdiI}} t^{\mathrm{adjk}} \lambda_{hp}^{\mathrm{Abjl}} \tag{A111}$$

$$0.25 g_{\mathrm{kl}} v_{\mathrm{bciI}} t_p^{\mathrm{ai}} t^{\mathrm{bcjk}} \lambda_{hp}^{\mathrm{aAjl}} \tag{A112}$$

$$-0.5 t^{\mathrm{aj}} v_{\mathrm{Abcj}} t_h^{\mathrm{ci}} \lambda_{hp}^{\mathrm{abiI}} \tag{A113}$$

$$0.5 g_{\mathrm{iI}} t^{\mathrm{bj}} t^{\mathrm{ck}} v_{\mathrm{aAcj}} \lambda_{hp'}^{\mathrm{abik}} \tag{A114}$$

$$-1. t^{\mathrm{cj}} v_{\mathrm{abcj}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A115}$$

$$-0.5 t^{\mathrm{bi}} v_{\mathrm{abcI}} t_h^{\mathrm{cj}} \lambda_{hp}^{\mathrm{aAij}} \tag{A116}$$

$$0.5 t^{\mathrm{aj}} v_{\mathrm{Acjk}} t_p^{\mathrm{bk}} t_h^{\mathrm{ci}} \lambda_{hp}^{\mathrm{abiI}} \tag{A117}$$

$$-1. t^{\mathrm{ck}} v_{\mathrm{bcjk}} t_p^{\mathrm{aj}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A118}$$

$$0.5 t^{\mathrm{bj}} v_{\mathrm{bciI}} t_p^{\mathrm{ai}} t_h^{\mathrm{ck}} \lambda_{hp}^{\mathrm{aAjk}} \tag{A119}$$

$$\lambda_b^j \langle_j^b | \bar{H} |_{IJ}^{AB} \rangle =$$

$$-1. v_{\mathrm{aABJ}} \lambda_h^{\mathrm{aI}} \tag{A120}$$

$$v_{\mathrm{aABI}} \lambda_h^{\mathrm{aJ}} \tag{A121}$$

$$v_{\mathrm{AiIJ}} \lambda_p^{\mathrm{Bi}} \tag{A122}$$

$$-1. v_{\mathrm{BiIJ}} \lambda_p^{\mathrm{Ai}} \tag{A123}$$

$$v_{\mathrm{ABiJ}} \lambda_h^{\mathrm{aI}} t_p^{\mathrm{ai}} \tag{A124}$$

$$-1. v_{\mathrm{ABiI}} \lambda_h^{\mathrm{aJ}} t_p^{\mathrm{ai}} \tag{A125}$$

$$-1. v_{\mathrm{aAIJ}} t_h^{\mathrm{ai}} \lambda_p^{\mathrm{Bi}} \tag{A126}$$

$$v_{\mathrm{aBIJ}} t_h^{\mathrm{ai}} \lambda_p^{\mathrm{Ai}} \tag{A127}$$

$$\lambda_{bc}^{jk} \langle_{jk}^{bc}|\bar{H}|_{IJ}^{AB}\rangle =$$

$$1. f_{\mathrm{aB}} g_{\mathrm{iJ}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A128}$$

$$-1. f_{\mathrm{aA}} g_{\mathrm{iJ}} \lambda_{hp}^{\mathrm{aBiI}} \tag{A129}$$

$$-1. g_{\mathrm{aB}} f_{\mathrm{iJ}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A130}$$

$$1. g_{\mathrm{aB}} f_{\mathrm{iI}} \lambda_{hp}^{\mathrm{aAiJ}} \tag{A131}$$

$$-1. f_{\mathrm{Bj}} g_{\mathrm{iJ}} t_p^{\mathrm{aj}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A132}$$

$$1. f_{\mathrm{Aj}} g_{\mathrm{iJ}} t_p^{\mathrm{aj}} \lambda_{hp}^{\mathrm{aBiI}} \tag{A133}$$

$$-1. f_{\mathrm{aJ}} g_{\mathrm{bB}} t_h^{\mathrm{ai}} \lambda_{hp}^{\mathrm{AbiI}} \tag{A134}$$

$$1. f_{\mathrm{aI}} g_{\mathrm{bB}} t_h^{\mathrm{ai}} \lambda_{hp}^{\mathrm{AbiJ}} \tag{A135}$$

$$0.5 g_{\mathrm{aA}} g_{\mathrm{bB}} v_{\mathrm{iIjJ}} r^{\mathrm{abij}} \tag{A136}$$

$$1. v_{\mathrm{aAiJ}} \lambda_{hp}^{\mathrm{aBiI}} \tag{A137}$$

$$-1. v_{\mathrm{aAiI}} \lambda_{hp}^{\mathrm{aBiJ}} \tag{A138}$$

$$-1. v_{\mathrm{aBiJ}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A139}$$

$$1. v_{\mathrm{aBiI}} \lambda_{hp}^{\mathrm{aAiJ}} \tag{A140}$$

$$0.5 g_{\mathrm{iI}} g_{\mathrm{jJ}} v_{\mathrm{aAbB}} r^{\mathrm{abij}} \tag{A141}$$

$$0.25 g_{\mathrm{bc}} g_{\mathrm{iJ}} v_{\mathrm{ABjk}} t^{\mathrm{acjk}} \lambda_{hp}^{\mathrm{abiI}} \tag{A142}$$

$$-0.5 g_{\mathrm{bc}} g_{\mathrm{ik}} v_{\mathrm{ABjJ}} t^{\mathrm{acjk}} \lambda_{hp}^{\mathrm{abiI}} \tag{A143}$$

$$0.5 g_{\mathrm{bc}} g_{\mathrm{ik}} v_{\mathrm{ABIj}} t^{\mathrm{acjk}} \lambda_{hp}^{\mathrm{abiJ}} \tag{A144}$$

$$0.5 g_{\mathrm{ab}} g_{\mathrm{iJ}} v_{\mathrm{Acjk}} t^{\mathrm{acjk}} \lambda_{hp}^{\mathrm{bBiI}} \tag{A145}$$

$$-1. v_{\mathrm{AbjJ}} t_{hp}^{\mathrm{abij}} \lambda_{hp}^{\mathrm{aBiI}} \tag{A146}$$

$$1. v_{\mathrm{AbIj}} t_{hp}^{\mathrm{abij}} \lambda_{hp}^{\mathrm{aBiJ}} \tag{A147}$$

$$0.5 g_{\mathrm{ab}} g_{\mathrm{jk}} v_{\mathrm{AcIJ}} t^{\mathrm{acij}} \lambda_{hp}^{\mathrm{bBik}} \tag{A148}$$

$$-0.5 g_{\mathrm{ab}} g_{\mathrm{iJ}} v_{\mathrm{Bcjk}} t^{\mathrm{acjk}} \lambda_{hp}^{\mathrm{AbiI}} \tag{A149}$$

$$1. v_{\mathrm{bBjJ}} \lambda_{hp}^{\mathrm{aAiI}} t_{hp}^{\mathrm{abij}} \tag{A150}$$

$$-1. v_{\mathrm{bBIj}} \lambda_{hp}^{\mathrm{aAiJ}} t_{hp}^{\mathrm{abij}} \tag{A151}$$

$$-0.5 g_{\mathrm{ab}} g_{\mathrm{jk}} v_{\mathrm{BcIJ}} t^{\mathrm{acij}} \lambda_{hp}^{\mathrm{Abik}} \tag{A152}$$

$$-0.5 g_{\mathrm{bB}} g_{\mathrm{ik}} v_{\mathrm{acjJ}} t^{\mathrm{acjk}} \lambda_{hp}^{\mathrm{AbiI}} \tag{A153}$$

$$0.5 g_{\mathrm{bB}} g_{\mathrm{ik}} v_{\mathrm{acIj}} t^{\mathrm{acjk}} \lambda_{hp}^{\mathrm{AbiJ}} \tag{A154}$$

$$0.25 g_{\mathrm{bB}} g_{\mathrm{jk}} v_{\mathrm{acIJ}} t^{\mathrm{acij}} \lambda_{hp}^{\mathrm{Abik}} \tag{A155}$$

$$-1. v_{\mathrm{AijJ}} t_p^{\mathrm{aj}} \lambda_{hp}^{\mathrm{aBiI}} \tag{A156}$$

$$1. v_{\mathrm{AiIj}} t_p^{\mathrm{aj}} \lambda_{hp}^{\mathrm{aBiJ}} \tag{A157}$$

$$1. v_{\mathrm{BijJ}} t_p^{\mathrm{aj}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A158}$$

$$-1. v_{\mathrm{BiIj}} t_p^{\mathrm{aj}} \lambda_{hp}^{\mathrm{aAiJ}} \tag{A159}$$

$$-1. g_{\mathrm{bB}} t^{\mathrm{aj}} v_{\mathrm{aijJ}} \lambda_{hp}^{\mathrm{AbiI}} \tag{A160}$$

$$1. g_{\mathrm{bB}} t^{\mathrm{aj}} v_{\mathrm{aiIj}} \lambda_{hp}^{\mathrm{AbiJ}} \tag{A161}$$

$$0.5 g_{\mathrm{Ab}} t^{\mathrm{aj}} v_{\mathrm{aiIJ}} \lambda_{hp'}^{\mathrm{bBij}} \tag{A162}$$

$$-0.5 g_{\mathrm{bB}} t^{\mathrm{ai}} v_{\mathrm{aIjJ}} \lambda_{hp}^{\mathrm{Abij}} \tag{A163}$$

$$-0.5 g_{\mathrm{iJ}} t^{\mathrm{aj}} v_{\mathrm{AbBj}} \lambda_{hp}^{\mathrm{abiI}} \tag{A164}$$

$$0.5 g_{\mathrm{iI}} t^{\mathrm{bj}} v_{\mathrm{aABj}} \lambda_{hp'}^{\mathrm{abiJ}} \tag{A165}$$

$$1. g_{\mathrm{iJ}} t^{\mathrm{bj}} v_{\mathrm{aAbj}} \lambda_{hp}^{\mathrm{aBiI}} \tag{A166}$$

$$-1. v_{\mathrm{aAbJ}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aBiI}} \tag{A167}$$

$$1. v_{\mathrm{aAbI}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aBiJ}} \tag{A168}$$

$$-1. g_{\mathrm{iJ}} t^{\mathrm{bj}} v_{\mathrm{abBj}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A169}$$

$$1. v_{\mathrm{abBJ}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A170}$$

$$-1. v_{\mathrm{abBI}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aAiJ}} \tag{A171}$$

$$0.5 g_{\mathrm{iJ}} t^{\mathrm{aj}} v_{\mathrm{ABjk}} t_p^{\mathrm{bk}} \lambda_{hp}^{\mathrm{abiI}} \tag{A172}$$

$$1. g_{\mathrm{iJ}} t^{\mathrm{bk}} v_{\mathrm{Abjk}} t_p^{\mathrm{aj}} \lambda_{hp}^{\mathrm{aBiI}} \tag{A173}$$

$$1. v_{\mathrm{AbjJ}} t_p^{\mathrm{aj}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aBiI}} \tag{A174}$$

$$-1. v_{\mathrm{AbIj}} t_p^{\mathrm{aj}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aBiJ}} \tag{A175}$$

$$-1. g_{\mathrm{iJ}} t^{\mathrm{bk}} v_{\mathrm{bBjk}} t_p^{\mathrm{aj}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A176}$$

$$-1. v_{\mathrm{bBjJ}} t_p^{\mathrm{aj}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aAiI}} \tag{A177}$$

$$1. v_{\mathrm{bBIj}} t_p^{\mathrm{aj}} t_h^{\mathrm{bi}} \lambda_{hp}^{\mathrm{aAiJ}} \tag{A178}$$

$$-1. g_{\mathrm{bB}} t^{\mathrm{cj}} v_{\mathrm{acjJ}} t_h^{\mathrm{ai}} \lambda_{hp}^{\mathrm{AbiI}} \tag{A179}$$

$$1. g_{\mathrm{bB}} t^{\mathrm{cj}} v_{\mathrm{acIj}} t_h^{\mathrm{ai}} \lambda_{hp}^{\mathrm{AbiJ}} \tag{A180}$$

$$0.5 g_{\mathrm{bB}} t^{\mathrm{ai}} v_{\mathrm{acIJ}} t_h^{\mathrm{cj}} \lambda_{hp}^{\mathrm{Abij}} \tag{A181}$$

3. $r^{(1)}$ equations and intermediates

$$\mathbf{H_{AI}^{q0}} =$$

$$f_{AI} \tag{A182}$$

$$f_{ai} t_{hp}^{aAiI} \tag{A183}$$

$$-1. f_{ai} t_h^{aI} t_p^{Ai} \tag{A184}$$

$$-0.5 g_{aA} v_{biIj} t^{abij} \tag{A185}$$

$$-0.5 g_{Ij} v_{aAbi} t^{abij} \tag{A186}$$

$$-1. t^{ai} v_{aAiI} \tag{A187}$$

$$-1. t^{aj} v_{aiIj} t_p^{Ai} \tag{A188}$$

$$-0.5 g_{aA} v_{bcij} t^{acij} t_h^{bI} \tag{A189}$$

$$t^{ai} v_{abij} t_{hp}^{AbIj} \tag{A190}$$

$$-0.5 g_{Ik} v_{abij} t^{abjk} t_p^{Ai} \tag{A191}$$

$$-1. t^{bi} v_{aAbi} t_h^{aI} \tag{A192}$$

$$-1. t^{bj} v_{abij} t_h^{aI} t_p^{Ai} \tag{A193}$$

$$\mathbf{H}^{\mathbf{q0}}_{\mathbf{ABIJ}} =$$

$$-1.g_{\mathrm{aB}}a_{\mathrm{IJ}}f_{\mathrm{bi}}t_h^{\mathrm{bJ}}t_{hp}^{\mathrm{aAiI}} \tag{A194}$$

$$-1.f_{\mathrm{ai}}a_{\mathrm{AB}}g_{\mathrm{jJ}}t_p^{\mathrm{Bi}}t_{hp}^{\mathrm{aAIj}} \tag{A195}$$

$$v_{\mathrm{ABIJ}} \tag{A196}$$

$$0.5v_{\mathrm{iIjJ}}t_{pp}^{\mathrm{ABij}} \tag{A197}$$

$$-1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aAiI}}t_{hp}^{\mathrm{aBiJ}} \tag{A198}$$

$$0.5v_{\mathrm{aAbB}}t_h^{\mathrm{abIJ}} \tag{A199}$$

$$a_{\mathrm{AB}}v_{\mathrm{AiIJ}}t_p^{\mathrm{Bi}} \tag{A200}$$

$$a_{\mathrm{IJ}}v_{\mathrm{aABI}}t_h^{\mathrm{aJ}} \tag{A201}$$

$$-1.a_{\mathrm{AB}}v_{\mathrm{abij}}t_{hp}^{\mathrm{aBiI}}t_{hp}^{\mathrm{AbjJ}} \tag{A202}$$

$$0.25v_{\mathrm{abij}}t_h^{\mathrm{abIJ}}t_{pp}^{\mathrm{ABij}} \tag{A203}$$

$$-0.5g_{\mathrm{aB}}g_{\mathrm{Jk}}v_{\mathrm{bcij}}t^{\mathrm{bcjk}}t_{hp}^{\mathrm{aAiI}} \tag{A204}$$

$$-0.5g_{\mathrm{aB}}a_{\mathrm{AB}}g_{\mathrm{Jk}}v_{\mathrm{bcij}}t^{\mathrm{acij}}t_{hp}^{\mathrm{AbIk}} \tag{A205}$$

$$-0.5g_{\mathrm{aB}}g_{\mathrm{Ik}}v_{\mathrm{bcij}}t^{\mathrm{bcik}}t_{hp}^{\mathrm{aAjJ}} \tag{A206}$$

$$v_{\mathrm{iIjJ}}t_p^{\mathrm{Ai}}t_p^{\mathrm{Bj}} \tag{A207}$$

$$a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aiIj}}t_p^{\mathrm{Bi}}t_{hp}^{\mathrm{aAjJ}} \tag{A208}$$

$$0.5a_{\mathrm{IJ}}v_{\mathrm{aiIj}}t_h^{\mathrm{aJ}}t_{pp}^{\mathrm{ABij}} \tag{A209}$$

$$-1.g_{\mathrm{aB}}a_{\mathrm{IJ}}t^{\mathrm{bi}}v_{\mathrm{biIj}}t_{hp}^{\mathrm{aAjJ}} \tag{A210}$$

$$a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aAiI}}t_h^{\mathrm{aJ}}t_p^{\mathrm{Bi}} \tag{A211}$$

$$0.5a_{\mathrm{AB}}v_{\mathrm{aAbi}}t_p^{\mathrm{Bi}}t_h^{\mathrm{abIJ}} \tag{A212}$$

$$a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aAbi}}t_h^{\mathrm{aJ}}t_{hp}^{\mathrm{bBiI}} \tag{A213}$$

$$-1.a_{\mathrm{AB}}g_{\mathrm{jJ}}t^{\mathrm{ai}}v_{\mathrm{aAbi}}t_{hp}^{\mathrm{bBIj}} \tag{A214}$$

$$v_{\mathrm{aAbB}}t_h^{\mathrm{aI}}t_h^{\mathrm{bJ}} \tag{A215}$$

$$a_{\mathrm{IJ}}v_{\mathrm{aiIj}}t_h^{\mathrm{aJ}}t_p^{\mathrm{Ai}}t_p^{\mathrm{Bj}} \tag{A216}$$

$$0.5v_{\mathrm{abij}}t_p^{\mathrm{Ai}}t_p^{\mathrm{Bj}}t_h^{\mathrm{abIJ}} \tag{A217}$$

$$-1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{abij}}t_h^{\mathrm{aJ}}t_p^{\mathrm{Bi}}t_{hp}^{\mathrm{AbIj}} \tag{A218}$$

$$-1.a_{\text{AB}}g_{\text{Jk}}t^{\text{ai}}v_{\text{abij}}t_p^{\text{Bj}}t_{hp}^{\text{AbIk}} \tag{A219}$$

$$0.5v_{\text{abij}}t_h^{\text{aI}}t_h^{\text{bJ}}t_{pp}^{\text{ABij}} \tag{A220}$$

$$g_{\text{aB}}a_{\text{IJ}}t^{\text{ci}}v_{\text{bcij}}t_h^{\text{bJ}}t_{hp}^{\text{aAIj}} \tag{A221}$$

$$a_{\text{AB}}v_{\text{aAbi}}t_h^{\text{aI}}t_h^{\text{bJ}}t_p^{\text{Bi}} \tag{A222}$$

$$v_{\text{abij}}t_h^{\text{aI}}t_p^{\text{Ai}}t_h^{\text{bJ}}t_p^{\text{Bj}} \tag{A223}$$

$\langle^A_I|\bar{H}|^a_i\rangle r^i_a =$

$$f_{\text{aA}}r_h^{\text{aI}} \tag{A224}$$

$$-1.f_{\text{iI}}r_p^{\text{Ai}} \tag{A225}$$

$$-1.f_{\text{ai}}r_h^{\text{aI}}t_p^{\text{Ai}} \tag{A226}$$

$$-1.f_{\text{ai}}t_h^{\text{aI}}r_p^{\text{Ai}} \tag{A227}$$

$$-1.r^{\text{ai}}v_{\text{aAiI}} \tag{A228}$$

$$-0.5g_{\text{aA}}v_{\text{bcij}}t^{\text{acij}}r_h^{\text{bI}} \tag{A229}$$

$$r^{\text{ai}}v_{\text{abij}}t_{hp}^{\text{AbIj}} \tag{A230}$$

$$-0.5g_{\text{Ik}}v_{\text{abij}}t^{\text{abjk}}r_p^{\text{Ai}} \tag{A231}$$

$$r^{\text{ai}}v_{\text{aiIj}}t_p^{\text{Aj}} \tag{A232}$$

$$-1.t^{\text{aj}}v_{\text{aiIj}}r_p^{\text{Ai}} \tag{A233}$$

$$-1.t^{\text{bi}}v_{\text{aAbi}}r_h^{\text{aI}} \tag{A234}$$

$$r^{\text{ai}}v_{\text{aAbi}}t_h^{\text{bI}} \tag{A235}$$

$$-1.t^{\text{bj}}v_{\text{abij}}r_h^{\text{aI}}t_p^{\text{Ai}} \tag{A236}$$

$$-1.t^{\text{bj}}v_{\text{abij}}t_h^{\text{aI}}r_p^{\text{Ai}} \tag{A237}$$

$$-1.r^{\text{ai}}v_{\text{abij}}t_p^{\text{Aj}}t_h^{\text{bI}} \tag{A238}$$

$$\langle {}^A_I | \bar{H} |^{bc}_{jk} \rangle r^{jk}_{bc} =$$

$$1. f_{\mathrm{ai}} r^{\mathrm{aAiI}}_{hp} \tag{A239}$$

$$-0.5 g_{\mathrm{aA}} v_{\mathrm{biIj}} r^{\mathrm{abij}} \tag{A240}$$

$$-0.5 g_{\mathrm{Ij}} v_{\mathrm{aAbi}} r^{\mathrm{abij}} \tag{A241}$$

$$0.5 g_{\mathrm{Ik}} v_{\mathrm{abij}} r^{\mathrm{abik}} t^{\mathrm{Aj}}_{p} \tag{A242}$$

$$1. t^{\mathrm{bj}} v_{\mathrm{abij}} r^{\mathrm{aAiI}}_{hp} \tag{A243}$$

$$0.5 g_{\mathrm{aA}} v_{\mathrm{bcij}} r^{\mathrm{abij}} t^{\mathrm{cI}}_{h} \tag{A244}$$

$$\langle {}^{AB}_{IJ}|\bar{H}|{}^{b}_{j}\rangle r^{j}_{b} =$$

$$-1.g_{\mathrm{aB}}a_{\mathrm{IJ}}f_{\mathrm{bi}}r^{\mathrm{bJ}}_{h}t^{\mathrm{aAiI}}_{hp} \tag{A245}$$

$$-1.f_{\mathrm{ai}}a_{\mathrm{AB}}g_{\mathrm{jJ}}r^{\mathrm{Bi}}_{p}t^{\mathrm{aAIj}}_{hp} \tag{A246}$$

$$a_{\mathrm{AB}}v_{\mathrm{AiIJ}}r^{\mathrm{Bi}}_{p} \tag{A247}$$

$$a_{\mathrm{IJ}}v_{\mathrm{aABI}}r^{\mathrm{aJ}}_{h} \tag{A248}$$

$$a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aiIj}}r^{\mathrm{Bi}}_{p}t^{\mathrm{aAjJ}}_{hp} \tag{A249}$$

$$0.5a_{\mathrm{IJ}}v_{\mathrm{aiIj}}r^{\mathrm{aJ}}_{h}t^{\mathrm{ABij}}_{pp} \tag{A250}$$

$$-1.g_{\mathrm{aB}}a_{\mathrm{IJ}}r^{\mathrm{bi}}v_{\mathrm{biIj}}t^{\mathrm{aAjJ}}_{hp} \tag{A251}$$

$$0.5a_{\mathrm{AB}}v_{\mathrm{aAbi}}r^{\mathrm{Bi}}_{p}t^{\mathrm{abIJ}}_{h} \tag{A252}$$

$$a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aAbi}}r^{\mathrm{aJ}}_{h}t^{\mathrm{bBiI}}_{hp} \tag{A253}$$

$$-1.a_{\mathrm{AB}}g_{\mathrm{jJ}}r^{\mathrm{ai}}v_{\mathrm{aAbi}}t^{\mathrm{bBIj}}_{hp} \tag{A254}$$

$$-1.a_{\mathrm{AB}}v_{\mathrm{iIjJ}}t^{\mathrm{Aj}}_{p}r^{\mathrm{Bi}}_{p} \tag{A255}$$

$$a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aAiI}}t^{\mathrm{aJ}}_{h}r^{\mathrm{Bi}}_{p} \tag{A256}$$

$$a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aAiI}}r^{\mathrm{aJ}}_{h}t^{\mathrm{Bi}}_{p} \tag{A257}$$

$$-1.a_{\mathrm{IJ}}v_{\mathrm{aAbB}}r^{\mathrm{aJ}}_{h}t^{\mathrm{bI}}_{h} \tag{A258}$$

$$-1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aiIj}}t^{\mathrm{aJ}}_{h}t^{\mathrm{Aj}}_{p}r^{\mathrm{Bi}}_{p} \tag{A259}$$

$$a_{\mathrm{IJ}}v_{\mathrm{aiIj}}r^{\mathrm{aJ}}_{h}t^{\mathrm{Ai}}_{p}t^{\mathrm{Bj}}_{p} \tag{A260}$$

$$-0.5a_{\mathrm{AB}}v_{\mathrm{abij}}t^{\mathrm{Aj}}_{p}r^{\mathrm{Bi}}_{p}t^{\mathrm{abIJ}}_{h} \tag{A261}$$

$$-1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{abij}}t^{\mathrm{aJ}}_{h}r^{\mathrm{Bi}}_{p}t^{\mathrm{AbIj}}_{hp} \tag{A262}$$

$$-1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{abij}}r^{\mathrm{aJ}}_{h}t^{\mathrm{Bi}}_{p}t^{\mathrm{AbIj}}_{hp} \tag{A263}$$

$$a_{\mathrm{AB}}g_{\mathrm{Jk}}t^{\mathrm{aj}}v_{\mathrm{abij}}r^{\mathrm{Bi}}_{p}t^{\mathrm{AbIk}}_{hp} \tag{A264}$$

$$-1.a_{\mathrm{AB}}g_{\mathrm{Jk}}r^{\mathrm{ai}}v_{\mathrm{abij}}t^{\mathrm{Bj}}_{p}t^{\mathrm{AbIk}}_{hp} \tag{A265}$$

$$-0.5a_{\mathrm{IJ}}v_{\mathrm{abij}}r^{\mathrm{aJ}}_{h}t^{\mathrm{bI}}_{h}t^{\mathrm{ABij}}_{pp} \tag{A266}$$

$$g_{\mathrm{aB}}a_{\mathrm{IJ}}t^{\mathrm{ci}}v_{\mathrm{bcij}}r^{\mathrm{bJ}}_{h}t^{\mathrm{aAIj}}_{hp} \tag{A267}$$

$$-1.g_{\mathrm{aB}}a_{\mathrm{IJ}}r^{\mathrm{bi}}v_{\mathrm{bcij}}t^{\mathrm{cJ}}_{h}t^{\mathrm{aAIj}}_{hp} \tag{A268}$$

$$a_{\mathrm{AB}}v_{\mathrm{aAbi}}t^{\mathrm{aI}}_{h}t^{\mathrm{bJ}}_{h}r^{\mathrm{Bi}}_{p} \tag{A269}$$

$$-1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aAbi}}r^{\mathrm{aJ}}_{h}t^{\mathrm{bI}}_{h}t^{\mathrm{Bi}}_{p} \tag{A270}$$

$$-1.a_{\mathrm{AB}}v_{\mathrm{abij}}t^{\mathrm{aI}}_{h}t^{\mathrm{Aj}}_{p}t^{\mathrm{bJ}}_{h}r^{\mathrm{Bi}}_{p} \tag{A271}$$

$$-1.a_{\mathrm{IJ}}v_{\mathrm{abij}}r^{\mathrm{aJ}}_{h}t^{\mathrm{Ai}}_{p}t^{\mathrm{bI}}_{h}t^{\mathrm{Bj}}_{p} \tag{A272}$$

$$\langle^{AB}_{IJ}|\bar{H}|^{bc}_{jk}\rangle r^{jk}_{bc} =$$

$$-1.g_{\mathrm{aB}}a_{\mathrm{IJ}}f_{\mathrm{iJ}}r^{\mathrm{aAiI}}_{hp} \tag{A273}$$

$$1.f_{\mathrm{aB}}a_{\mathrm{AB}}g_{\mathrm{iJ}}r^{\mathrm{aAiI}}_{hp} \tag{A274}$$

$$1.g_{\mathrm{aB}}a_{\mathrm{IJ}}f_{\mathrm{bi}}t^{\mathrm{bI}}_{h}r^{\mathrm{aAiJ}}_{hp} \tag{A275}$$

$$1.f_{\mathrm{ai}}a_{\mathrm{AB}}g_{\mathrm{jJ}}t^{\mathrm{Ai}}_{p}r^{\mathrm{aBIj}}_{hp} \tag{A276}$$

$$0.5g_{\mathrm{aA}}g_{\mathrm{bB}}v_{\mathrm{iIjJ}}r^{\mathrm{abij}} \tag{A277}$$

$$-1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aAiI}}r^{\mathrm{aBiJ}}_{hp} \tag{A278}$$

$$0.5g_{\mathrm{iI}}g_{\mathrm{jJ}}v_{\mathrm{aAbB}}r^{\mathrm{abij}} \tag{A279}$$

$$1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{abij}}r^{\mathrm{aBiJ}}_{hp}t^{\mathrm{AbIj}}_{hp} \tag{A280}$$

$$0.25g_{\mathrm{Ik}}g_{\mathrm{Jl}}v_{\mathrm{abij}}r^{\mathrm{abkl}}t^{\mathrm{ABij}}_{pp} \tag{A281}$$

$$-0.5g_{\mathrm{aB}}a_{\mathrm{AB}}g_{\mathrm{Jk}}v_{\mathrm{bcij}}t^{\mathrm{acij}}r^{\mathrm{AbIk}}_{hp} \tag{A282}$$

$$-0.5g_{\mathrm{aB}}a_{\mathrm{IJ}}g_{\mathrm{Jk}}v_{\mathrm{bcij}}t^{\mathrm{bcjk}}r^{\mathrm{aAiI}}_{hp} \tag{A283}$$

$$0.5g_{\mathrm{aB}}a_{\mathrm{IJ}}g_{\mathrm{Jk}}v_{\mathrm{bcij}}r^{\mathrm{bcik}}t^{\mathrm{aAIj}}_{hp} \tag{A284}$$

$$0.5g_{\mathrm{aB}}a_{\mathrm{AB}}g_{\mathrm{Jk}}v_{\mathrm{bcij}}r^{\mathrm{abij}}t^{\mathrm{AcIk}}_{hp} \tag{A285}$$

$$0.25g_{\mathrm{aA}}g_{\mathrm{bB}}v_{\mathrm{cdij}}r^{\mathrm{abij}}t^{\mathrm{cdIJ}}_{h} \tag{A286}$$

$$1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aiIj}}t^{\mathrm{Aj}}_{p}r^{\mathrm{aBiJ}}_{hp} \tag{A287}$$

$$1.g_{\mathrm{aB}}a_{\mathrm{IJ}}t^{\mathrm{bj}}v_{\mathrm{biIj}}r^{\mathrm{aAiJ}}_{hp} \tag{A288}$$

$$0.5g_{\mathrm{aA}}a_{\mathrm{IJ}}g_{\mathrm{bB}}v_{\mathrm{ciIj}}r^{\mathrm{abij}}t^{\mathrm{cJ}}_{h} \tag{A289}$$

$$1.a_{\mathrm{AB}}g_{\mathrm{jJ}}t^{\mathrm{bi}}v_{\mathrm{aAbi}}r^{\mathrm{aBIj}}_{hp} \tag{A290}$$

$$0.5a_{\mathrm{AB}}g_{\mathrm{Ij}}g_{\mathrm{Jk}}v_{\mathrm{aAbi}}r^{\mathrm{abjk}}t^{\mathrm{Bi}}_{p} \tag{A291}$$

$$1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{aAbi}}t^{\mathrm{bI}}_{h}r^{\mathrm{aBiJ}}_{hp} \tag{A292}$$

$$1.a_{\mathrm{AB}}g_{\mathrm{Jk}}t^{\mathrm{bj}}v_{\mathrm{abij}}t^{\mathrm{Ai}}_{p}r^{\mathrm{aBIk}}_{hp} \tag{A293}$$

$$-1.a_{\mathrm{AB}}a_{\mathrm{IJ}}v_{\mathrm{abij}}t^{\mathrm{Aj}}_{p}t^{\mathrm{bI}}_{h}r^{\mathrm{aBiJ}}_{hp} \tag{A294}$$

$$0.5g_{\mathrm{Ik}}g_{\mathrm{Jl}}v_{\mathrm{abij}}r^{\mathrm{abkl}}t^{\mathrm{Ai}}_{p}t^{\mathrm{Bj}}_{p} \tag{A295}$$

$$1.g_{\mathrm{aB}}a_{\mathrm{IJ}}t^{\mathrm{cj}}v_{\mathrm{bcij}}t^{\mathrm{bI}}_{h}r^{\mathrm{aAiJ}}_{hp} \tag{A296}$$

$$0.5g_{\mathrm{aA}}g_{\mathrm{bB}}v_{\mathrm{cdij}}r^{\mathrm{abij}}t^{\mathrm{cI}}_{h}t^{\mathrm{dJ}}_{h} \tag{A297}$$

Appendix B: A24 binding energies

complex / model	$\{ijab\}$	$\{ijab\}+\{i\}\{a\}$	$\{ia\}\{jb\}$	$\{ia\}\{jb\}+\{i\}\{a\}$	$\{i\}\{j\}\{a\}\{b\}$	MP2	CCSD
01 water ... ammonia	-21.48	-24.37	-22.36	-25.29	-26.84	-29.10	-27.09
02 water dimer	-17.25	-19.09	-17.92	-19.72	-20.72	-21.94	-20.93
03 HCN dimer	-19.38	-20.31	-19.85	-20.81	-21.60	-23.57	-21.90
04 HF dimer	-15.99	-17.79	-16.50	-18.30	-19.05	-19.30	-19.09
05 ammonia dimer	-10.47	-11.30	-11.14	-11.97	-12.90	-14.15	-12.94
06 HF ... methane	-5.53	-5.86	-6.07	-6.45	-6.91	-7.79	-7.08
07 ammonia ... methane	-3.14	-3.52	-3.52	-3.85	-4.31	-4.77	-4.40
08 water ... methane	-2.68	-2.89	-2.97	-3.14	-3.48	-3.85	-3.52
09 formaldehyde dimer	-12.69	-14.99	-13.61	-15.99	-18.34	-20.18	-18.30
10 water ... ethene	-8.79	-9.63	-9.46	-10.30	-11.10	-13.44	-11.43
11 formaldehyde ... ethene	-5.95	-6.24	-6.53	-6.82	-7.70	-9.13	-7.79
12 ethyne dimer	-6.70	-7.12	-7.12	-7.54	-7.95	-9.84	-8.37
13 ammonia ... ethene	-5.36	-5.78	-5.86	-6.24	-6.78	-8.58	-7.08
14 ethene dimer	-4.27	-4.56	-4.94	-5.23	-5.86	-8.25	-6.24
15 methane ... ethene	-2.51	-2.64	-2.81	-2.97	-3.43	-4.23	-3.48
16 borane ... methane	-2.43	-3.27	-3.64	-4.52	-5.53	-7.24	-5.95
17 methane ... ethane	-3.64	-3.64	-4.31	-4.31	-4.69	-5.86	-5.02
18 methane ... ethane	-3.10	-3.10	-3.64	-3.64	-4.02	-4.65	-4.14
19 methane dimer	-2.68	-2.64	-3.10	-3.10	-3.48	-3.98	-3.52
20 Ar ... methane	-1.30	-1.30	-1.51	-1.55	-1.72	-2.34	-1.97
21 Ar ... ethene	-0.67	-0.71	-0.84	-0.88	-1.09	-1.88	-1.26
22 ethene ... ethyne	4.48	4.61	4.06	4.19	3.39	0.54	3.22
23 ethene dimer	4.61	4.73	4.06	4.19	3.18	0.59	3.06
24 ethyne dimer	5.82	5.95	5.48	5.61	4.94	1.93	4.81

TABLE IX: A24 binding energies in kJ/mol for fully-non-orthogonal truncation models and canonical MP2 and CCSD computed in aug-cc-pVDZ using the frozen core approximation. The horizontal lines delineate sets of hydrogen-bonded, mixed-character, and dispersion-dominated interactions.