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A nondiagonal quasidegenerate fourth-order perturbation theory

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A canonical quasidegenerate Rayleigh-Schrödinger perturbation theory, correct through fourth order in the energy, is explored for a block-diagonal unperturbed Hamiltonian. The theory is developed completely within a Lie Algebra in Hilbert space. Explicit equations for n-particle transition elements in terms of solutions of simultaneous linear equations are presented. A two-dimensional anisotropic anharmonic oscillator is used to provide numerical results. The perturbation theory is shown to be stable under small separation of model and complement spaces. An iterative variant of the fourth-order perturbation theory is introduced; the iterative variant is related to the non-iterative one in much the same way as nondegenerate coupled cluster theories are related to nondegenerate perturbation theory. The quasidegenerate coupled cluster theory appears to be stable in the presence of multiple intruder states.

1. Introduction

The realization of ever more efficacious approximation methods for solutions of the time-independent Schrödinger equation remains an important goal in the physical sciences. Quasidegenerate perturbation theories (QDPT), including iterative approximations of the coupled cluster variety, remain an especially lucrative methodology. For recent reviews of QDPT, see refs. [1] and [2]. Quasidegenerate perturbation theories have been developed and successfully applied to a number of problems in nuclear [3–6], atomic [7–9] and molecular [10–20] physics. Nonetheless, difficulties remain with routine application of QDPT, especially with the ability to describe reliably excited states and to treat weakly quasidegenerate systems on an equal footing with strongly quasidegenerate systems.

In this paper, we present a *nondiagonal* Rayleigh-Schrödinger QDPT correct through fourth order in the effective Hamiltonian that uses a novel intermediate Hamiltonian to avoid numerical instabilities due to so-called intruder states [3]. The matrix formulation is described herein; i.e., explicit equations are given in terms of n-particle transition amplitudes. An iterative approximation to the fourth-order effective Hamiltonian, that is similar to the relation that nondegenerate

coupled cluster methods have to nondegenerate perturbation theory, is also presented. We investigate numerically characteristics of the proposed theories with calculations on coupled, anisotropic anharmonic Hamiltonians of the form

$$\hat{H}(x,y) = \tfrac{1}{2}\hat{p}_x^2 + \tfrac{1}{2}\hat{p}_y^2 + \tfrac{1}{2}k_x\hat{x}^2 + \tfrac{1}{2}k_y\hat{y}^2 + a\hat{x}\hat{y} + b\hat{x}^4\,, \tag{1}$$

which may also, in coordinate representation, be written as

$$H(\xi,\eta) = \hbar\omega\left\{\frac{1}{2}(1+\gamma)\left(\frac{-\partial^2}{\partial\xi^2}+\xi^2\right) + \frac{1}{2}(1-\gamma)\left(\frac{-\partial^2}{\partial\eta^2}+\eta^2\right) + \frac{a}{k}\sqrt{\frac{1}{(1+\gamma)(1-\gamma)}}\xi\eta + \frac{1}{(1+\gamma)^2}\left(\frac{b}{k\beta^2}\right)\xi^4\right\}. \tag{2}$$

The anisotropy, γ, and mean force constant, k, are defined through $k_x = k(l+\gamma)^2$ and $k_y = k(l-\gamma)^2$; the unit of energy is defined through the mean frequency $\omega = \sqrt{k/m}$. The length scales are defined by $\beta_x^2 = \sqrt{k_x m}/\hbar$, $\beta_y^2 = \sqrt{k_y m}/\hbar$, and $\beta^2 = \sqrt{km}/\hbar$; the scaled coordinates are $\xi = \beta_x x$ and $\eta = \beta_y y$.

Quasidegenerate methods are based on the observation that an exact eigenfunction of the Hamiltonian can be generated from a reference function in a subspace of the full Hilbert space by the action of a wave operator [21],

$$|\Psi_\alpha\rangle = \Omega|\tilde{\Phi}_\alpha\rangle\,. \tag{3}$$

The domain of the wave operator partitions Hilbert space into two subspaces: the model space and its orthogonal complement. The relation of the model space wavefunction and the exact wavefunction given in eq. (3) implies a similarity transformation of the Hamiltonian; i.e.,

$$H^{eff} = \Omega^{-1}H\Omega\,. \tag{4}$$

The effective Hamiltonian acts on a function in the model space to produce the exact energies,

$$H^{eff}|\tilde{\Phi}_\alpha\rangle = E_\alpha|\tilde{\Phi}_\alpha\rangle\,. \tag{5}$$

The reference functions of eqs. (3) and (5) have been referred to as the "bonne functions" (cf. refs. [22–24]). The bonne functions are, of course, expressible as a linear combination of model space basis functions: $|\tilde{\Phi}_\alpha\rangle = \sum_a C_a^\alpha|\Phi_\alpha\rangle$.

Eq. (4) may be rewritten as

$$\Omega H^{eff} = H\Omega\,. \tag{6}$$

In order to solve the above equation, it is convenient to introduce the projector on the model space,

$$P = \sum_{a\in\mathcal{P}}|\Phi_a\rangle\langle\Phi_a| \tag{7}$$

and the projector on the complement space,

$$Q = \sum_{n \in Q} |\Phi_n\rangle\langle\Phi_n| \,. \tag{8}$$

The summation in eq. (7) is over the d-dimensional subspace $\mathcal{P}$ of Hilbert space that is used to define the model space; in eq. (8), the summation is over all of Hilbert space complementary to subspace $\mathcal{P}$. As demonstrated by Shavitt and Redmon [13] (also see refs. [23,24]), eq. (6) rearranges to

$$H_D \Omega_X = -H_X \Omega_D + \Omega_X H_D^{eff} \,, \tag{9}$$

where the block diagonal and off-diagonal parts of the Hamiltonian and wave operator have been defined by

$$A_D = PAP + QAQ \tag{10a}$$

and

$$A_X = PAQ + QAP \,. \tag{10b}$$

Eq. (9) may be considered the fundamental equation for developing any effective Hamiltonian.

2. Quasidegenerate perturbation theory

Several major variants of QDPT have been defined [13,25,26]; our development is of the canonical formulation variety. The canonical formulation is most conveniently expressed in terms of the logarithm of the wave operator,

$$|\Psi_\alpha\rangle = e^G |\tilde{\Phi}_\alpha\rangle \,. \tag{11}$$

The canonical variant of QDPT is defined by the requirement that the block diagonal part of the logarithm of the wave operator vanish, i.e., $G_D = 0$, and that $G_X = -G^\dagger$. The logarithm of the wave operator and the effective Hamiltonian may be expanded as power series, i.e.,

$$G = G^{(1)} + G^{(2)} + G^{(3)} + \ldots \tag{12}$$

and

$$H^{eff} = H_0 + W_D^{(1)} + W_D^{(2)} + W_D^{(3)} + W_D^{(4)} + \ldots \,. \tag{13}$$

Substituting the perturbative series into eq. (9) and using a power expansion of e^G yields the individual order perturbation equations [13].

Our nondiagonal quasidegenerate perturbation theory is developed from an unperturbed Hamiltonian with the following structure:

$$H_0 = PHP + Q_1 H Q_1 + Q_2 H Q_2 + \ldots \,. \tag{14}$$

In eq. (14) the complement space, $\mathcal{Q}$, is further partitioned by the minimum number of mappings that a set of functions are removed from the model space; for example, for any function, $|\Phi_{q_2}\rangle$, in the $\mathcal{Q}_2$ subspace and function $|\Phi_a\rangle$ in $\mathcal{P}$, $\langle\Phi_a|H|\Phi_{q_2}\rangle = 0$. Fig. 1 illustrates the structure of the Hamiltonian, with crosshatched regions included in H_0, striped regions containing potentially nonzero matrix elements, and all blank regions rigorously zero. A perturbative evaluation of the eigenvalues and model space eigenvectors of the Hamiltonian may now be developed from the above specified H_0.

Computational implementation of the proposed quasidegenerate perturbation theory could be realized through explicit formulas involving model space matrix elements of products of creation and annihilation operators, or, equivalently, by diagrammatic techniques. An alternative approach is the matrix formulation [12,21]: the required transition matrix elements of $G^{(1)}$ can be obtained as

$$\sum_m \langle\Phi_n|H|\Phi_m\rangle\langle\Phi_m|G^{(1)}|\Phi_a\rangle - \sum_c \langle\Phi_n|G^{(1)}|\Phi_c\rangle\langle\Phi_c|H|\Phi_a\rangle = -\langle\Phi_n|H|\Phi_a\rangle\,. \tag{15}$$

The first summation is over the set of all, the previously discussed, no-more-than-singly-excited basis functions ($\mathcal{Q}_1$); the second summation is over all model space functions. The set of necessary bra functions, $|\Phi_n\rangle$, is a basis of $\mathcal{Q}_1$.

The second-order correction to the effective Hamiltonian can be expressed directly in terms of the $G^{(1)}$ matrix elements from eq. (15) and Hamiltonian matrix elements,

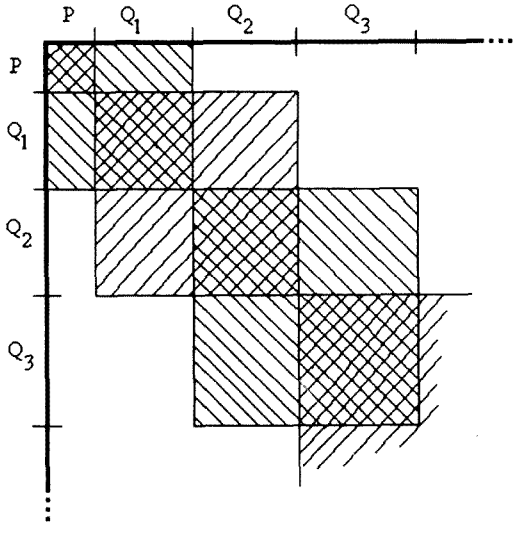

Fig. 1.

$$\langle\Phi_a|W_D^{(2)}|\Phi_b\rangle = \tfrac{1}{2}\langle\Phi_a|[H_X, G_X^{(1)}]|\Phi_b\rangle$$
$$= \tfrac{1}{2}\sum_d \{\langle\Phi_a|H|\Phi_d\rangle\langle\Phi_d|G^{(1)}|\Phi_b\rangle - \langle\Phi_a|G^{(1)}|\Phi_d\rangle\langle\Phi_d|H|\Phi_b\rangle\}\,. \tag{16}$$

In eq. (16), the summation is restricted, without approximation, to complement space basis functions that are no-more-than-singly excited relative to either model space function $|\Phi_a\rangle$ or $|\Phi_b\rangle$.

Though our complement space basis functions are not eigenfunctions of H_0, it proves convenient to rotate our basis in the model space so that the model space basis functions are eigenfunctions of H_0:

$$H_0|\Phi_a^0\rangle = E_a^1|\Phi_a^0\rangle\,. \tag{17}$$

The diagonal part of the Hamiltonian is related to the zero-order Hamiltonian by

$$H_D = H_0 + V_D\,, \tag{18}$$

where $V_D = Q_1HQ_2 + Q_2HQ_1 + \ldots$. Hence, H_0 and H_D are identical in the model space, but not in the complement space. With the rotated basis in the model space, eq. (15) takes on the simpler, and more computational tractable, form,

$$\sum_{m\in Q_1}(\langle\Phi_n|H|\Phi_m\rangle - \delta_{mn}E_a^1)\langle\Phi_m|G^{(1)}|\Phi_a^0\rangle = -\langle\Phi_n|H|\Phi_a^0\rangle\,. \tag{19}$$

Neither eq. (16) nor (19) is surprising, and may be seen to be essentially multireference CEPA-0 equations [15,27,28]. While the purpose of the present work is to develop higher-than-second-order, nondiagonal, perturbation theories, it ought to be noted that substantial improvements in accuracy can be achieved in second order by more sophisticated treatments [29–32].

The equations for the second-order correction to the logarithm of the wave operator, $G^{(2)}$, are developed similarly to the first-order correction. One obtains

$$\sum_{m\in Q_2}(\langle\Phi_n|H|\Phi_m\rangle - \delta_{mn}E_a^1)\langle\Phi_m|G^{(2)}|\Phi_a^0\rangle$$
$$= -\sum_{k\in Q_1}\langle\Phi_n|H|\Phi_k\rangle\langle\Phi_k|G^{(1)}|\Phi_a^0\rangle\,, \tag{20}$$

where the $|\Phi_n\rangle \in Q_2$. However, one also obtains the result that the third-order correction to the effective Hamiltonian is rigorously zero with our partitioning, i.e., $\langle\Phi_a^0|W_D^{(3)}|\Phi_b^0\rangle = 0$. It ought to be noted that the second-order correction to the wavefunction is *not* equal to zero and, if calculation of fourth- or higher-order corrections to the effective Hamiltonian are required, the second-order corrections to the wavefunction must be calculated. Eq. (20) represents a substantial computa-

tional effort comparable to configuration interaction CISDTQ or coupled cluster CCSDTQ [33] approaches to molecular physics problems.

Evaluation of the equation for the third-order correction to the wave operator in a basis gives

$$\begin{aligned}
&\sum_{m\in\mathcal{Q}_1\oplus\mathcal{Q}_3}(\langle\Phi_n|H|\Phi_m\rangle-\delta_{mn}E_a^1)\langle\Phi_m|G^{(3)}|\Phi_a^0\rangle\\
&\quad=-\sum_{q\in\mathcal{Q}_2}\langle\Phi_n|V_D|\Phi_q\rangle\langle\Phi_q|G^{(2)}|\Phi_a^0\rangle\\
&\qquad-\frac{1}{3}\sum_{c\in\mathcal{P}}\langle\Phi_n|H|\Phi_c^0\rangle\sum_{m\in\mathcal{Q}_1}\langle\Phi_c^0|G^{(1)}|\Phi_m\rangle\langle\Phi_m|G^{(1)}|\Phi_a^0\rangle\\
&\qquad+\frac{2}{3}\sum_{c\in\mathcal{P}}\langle\Phi_n|G^{(1)}|\Phi_c^0\rangle\sum_{m\in\mathcal{Q}_1}\langle\Phi_c^0|H|\Phi_m\rangle\langle\Phi_m|G^{(1)}|\Phi_a^0\rangle\\
&\qquad-\frac{1}{3}\sum_{c\in\mathcal{P}}\langle\Phi_n|G^{(1)}|\Phi_c^0\rangle\sum_{m\in\mathcal{Q}_1}\langle\Phi_c^0|G^{(1)}|\Phi_m\rangle\langle\Phi_m|H|\Phi_a^0\rangle\,. \qquad (21)
\end{aligned}$$

The summation over complement space functions on the left hand side are rigorously over the union of $\mathcal{Q}_1$ and $\mathcal{Q}_3$ subspaces. The $\langle\Phi_n|$ are also rigorously restricted to the union of $\mathcal{Q}_1$ and $\mathcal{Q}_3$ subspaces; consequently, the above simultaneous equations decouple into $\mathcal{Q}_1\otimes\mathcal{Q}_1$ and $\mathcal{Q}_3\otimes\mathcal{Q}_3$ blocks. Model space matrix elements of the fourth-order correction to the effective Hamiltonian

$$W_D^{(4)}=\frac{1}{2}[H_X,G_X^{(3)}]-\frac{1}{24}[[[H_X,G_X^{(1)}],G_X^{(1)}],G_X^{(1)}] \qquad (22)$$

can be written, after some algebra, as

$$\begin{aligned}
&\langle\Phi_a^0|W_D^{(4)}|\Phi_b^0\rangle\\
&\quad=\frac{1}{2}\sum_{m\in\mathcal{Q}_1}\{\langle\Phi_m|H|\Phi_a^0\rangle\langle\Phi_m|G^{(3)}|\Phi_b^0\rangle+\langle\Phi_m|G^{(3)}|\Phi_a^0\rangle\langle\Phi_m|H|\Phi_b^0\rangle\}\\
&\qquad+\frac{1}{12}\sum_{c\in\mathcal{P}}\langle\Phi_a^0|W_D^{(2)}|\Phi_c^0\rangle\sum_{m\in\mathcal{Q}_1}\langle\Phi_m|G^{(1)}|\Phi_c^0\rangle\langle\Phi_m|G^{(1)}|\Phi_b^0\rangle\\
&\qquad+\frac{1}{12}\sum_{c\in\mathcal{P}}\langle\Phi_c^0|W_D^{(2)}|\Phi_b^0\rangle\sum_{m\in\mathcal{Q}_1}\langle\Phi_m|G^{(1)}|\Phi_a^0\rangle\langle\Phi_m|G^{(1)}|\Phi_c^0\rangle\\
&\qquad+\frac{1}{12}\sum_{m\in\mathcal{Q}_1}\langle\Phi_m|G^{(1)}|\Phi_a^0\rangle\sum_{c\in\mathcal{P}}\langle\Phi_m|G^{(1)}|\Phi_c^0\rangle\sum_{k\in\mathcal{Q}_1}\langle\Phi_k|H|\Phi_c^0\rangle\langle\Phi_k|G^{(1)}|\Phi_b^0\rangle\\
&\qquad+\frac{1}{12}\sum_{m\in\mathcal{Q}_1}\langle\Phi_m|G^{(1)}|\Phi_b^0\rangle\sum_{c\in\mathcal{P}}\langle\Phi_m|G^{(1)}|\Phi_c^0\rangle\sum_{k\in\mathcal{Q}_1}\langle\Phi_k|H|\Phi_c^0\rangle\langle\Phi_k|G^{(1)}|\Phi_a^0\rangle\,. \qquad (23)
\end{aligned}$$

Examination of eq. (23) shows that the $\mathcal{Q}_3$ matrix elements of $G^{(3)}$ are not needed

in fourth order in the effective Hamiltonian; hence, only solution of the $\mathcal{Q}_1 \otimes \mathcal{Q}_1$ block of eq. (21) is required.

3. Intermediate effective Hamiltonians

The concept of partitioning an effective or model Hamiltonian further into a subspace of interest and one that is uninteresting for the problem at hand has been proposed already by Löwdin [21]. This partitioning often can alleviate the intruder state problem [3]; intruder states are states outside the model space that have energy eigenvalues within the range of those of the model space. Partitioning has also proven to be computationally efficacious; the most computationally intensive parts of the construction of the effective Hamiltonian is then limited to the usually small primary block. Partitioning has been used in several formulations of quasidegenerate or multireference perturbation theories [8,14,34]. Malrieu and Daudey [8] introduced a form of partitioning in which *m exact* energies and projections of *m exact* eigenvectors of the *d*-dimensional model space are obtained at convergence; though their introduction of the phrase *intermediate Hamiltonian* originally referred to their particular form of partitioning, it has now found more general use. The intermediate Hamiltonian we propose for use with our quasidegenerate perturbation and coupled cluster theories is not of the Malrieu and Daudey type, and may be seen to be closer to that produced by the buffer space of Kirtman [14].

Our intermediate Hamiltonian is constructed by further division of the model space functions into a so-called primary subspace, $\mathcal{P}_0$, whose eigenvalues and eigenvectors are of interest, and a buffer subspace, $\mathcal{P}_1$, that is not of any particular interest. With a proper choice of primary states, the energetically high-lying functions in the model space are not perturbatively (or iteratively, for a coupled cluster approximation) improved, and, so, the potentially numerically ill-behaved remixing of these functions with the low-lying functions in the complement space does not destabilize the calculation.

We develop an intermediate Hamiltonian formulation in terms of a double perturbation theory, in which one of the perturbations is set to zero. Let P_0 be the projector onto the primary model space and P_1 be the projector onto the buffer subspace. Instead of the unperturbed Hamiltonian of eq. (14), we now take

$$H_0 = P_0HP_0 + P_1HP_1 + Q_1HQ_1 + Q_2HQ_2 + \ldots \tag{24}$$

and define

$$V_X^{(1)} = P_0HQ + QHP_0 \tag{25}$$

and

$$V_D^{(1)} = P_1HP_0 + P_0HP_1 + Q_1HQ_2 + Q_2HQ_1 + \ldots , \tag{26}$$

leaving

$$V_X^{(2)} = P_1 H Q + Q H P_1 \,. \tag{27}$$

In eqs. (25) and (27), we used the unsubscripted complement space projector, Q, defined as, $Q = Q_1 + Q_2 + Q_3 + \ldots$.

Our intermediate Hamiltonian is then developed by setting $V_X^{(2)}$ equal to zero. The equations for the transitions elements (e.g., eq. (19)) are unchanged in structure, but the range of the indices is reduced relative to the equations used for the full effective Hamiltonian. For example, eq. (19) is solved only for zero-order functions in the primary space and $\langle \Phi_m | G^{(1)} | \Phi_\mu^0 \rangle \equiv 0$, for $|\Phi_\mu^0\rangle \in \mathcal{P}_1$. Likewise, the summation in eq. (16) is reduced to be over only the primary subspace. Similar reductions in ranges of indices occur in the fourth-order equations and in coupled cluster (*vide infra*).

4. Quasidegenerate coupled cluster

The canonical variant of quasidegenerate perturbation theory was used in the finite order theories developed above. However, the particularly simple relation determining the correlation operator, χ, in the intermediate normalized variant [13,25,26],

$$[H_D, \chi] = -V_X + \chi V_X \chi \,, \tag{28}$$

makes this a more convenient starting point for developing an iterative solution. Without further modification, intermediate normalization yields a non-Hermitian effective Hamiltonian; so, we follow Kvasnicka [35] and use the Hermitian average. Our development of the coupled cluster approximation follows our perturbation treatment, other than the choice of normalization. In particular, the quasidegenerate coupled cluster theory is developed completely within a Lie algebra and, so, is expected to be size-extensive [36] up to small errors introduced by use of an intermediate Hamiltonian. It should be noted that rigorously size-extensive intermediate Hamiltonians have been formulated by Mukherjee and Kutzelnigg using a Fock space approach [37–39]. In the present, Hilbert-space, formulation, size-extensivity will depend on partitioning; however, a physically reasonable partitioning is expected to give no or physically insignificant size-extensivity errors.

In terms of the subspaces introduced above, the correlation operator may be written without approximation as

$$\begin{aligned} \chi = {} & P_0 \chi Q_1 + Q_1 \chi P_0 + P_0 \chi Q_2 + Q_2 \chi P_0 + \ldots \\ & + Q_1 \chi Q_2 + Q_2 \chi Q_1 + \ldots \\ & + P_1 \chi Q_1 + Q_1 \chi P_1 + P_1 \chi Q_2 + Q_2 \chi P + \ldots \,. \end{aligned} \tag{29}$$

We define our coupled cluster excitation operator as the sum of operators capable of acting directly between the primary subspace of the model space and the first- and second-excited complement spaces; i.e.,

$$\chi^{cc} \equiv \chi^{(1)} + \chi^{(2)} \tag{30a}$$

with

$$\chi^{(1)} \equiv P_0\chi Q_1 + Q_1\chi P_0 + Q_1\chi Q_2 + Q_2\chi Q_1 \tag{30b}$$

and

$$\chi^{(2)} \equiv P_0\chi Q_2 + Q_2\chi P_0 \,. \tag{30c}$$

Though an explicit representation (e.g., in terms of products of one-particle creation and annihilation operators and basis function projectors) of χ might be difficult or impractical to obtain, the n-particle matrix elements can readily be calculated. Notice that the meaning of the superscripts are different in eq. (30) than in the previous sections; in particular, no sense of "perturbative order" is implied in eq. (30).

A matrix representation of the correlation operator can be obtained by requiring that certain relations hold. One such requirement is that eq. (28) holds exactly for matrix elements between $\mathcal{Q}_1$ and $\mathcal{P}_0$ for the approximate correlation operator (cf. eq. (30)),

$$\langle\Phi_n|[H_D, \chi^{(1)} + \chi^{(2)}]|\Phi_a^0\rangle = \langle\Phi_n| - V_X + \chi^{(1)}V_X\chi^{(1)} + \chi^{(2)}V_X\chi^{(1)}|\Phi_a^0\rangle \,. \tag{31}$$

Decoupling occurs by requiring that the relation between the second- and first-order subspace parts of the coupled cluster operator maintain the structure relating the second- and first-order perturbation corrections; i.e.,

$$[H_0, \chi^{(2)}] = -[V_D, \chi^{(1)}] \,. \tag{32}$$

Substituting eq. (32) into eq. (31) yields our working quasidegenerate coupled cluster equations for $\chi^{(1)}$,

$$\begin{aligned}\sum_{m\in\mathcal{Q}_1} (\langle\Phi_n|H|\Phi_m\rangle - \delta_{mn}E_a^1)\langle\Phi_m|\chi^{(1)}|\Phi_a^0\rangle \\ = -\langle\Phi_n|V_X|\Phi_a^0\rangle - \sum_{m\in\mathcal{Q}_2}\langle\Phi_n|H|\Phi_m\rangle\langle\Phi_m|\chi^{(2)}|\Phi_a^0\rangle \\ + \sum_{c\in\mathcal{P}_0}\langle\Phi_n|\chi^{(1)}|\Phi_c^0\rangle\langle\Phi_c^0|V_X\chi^{(1)}|\Phi_a^0\rangle \,.\end{aligned} \tag{33}$$

It may be appreciated that the proposed theory is not "linearized". The $\chi^{(1)}$ excitation operator matrix elements appear on both sides of the equation; furthermore,

$\chi^{(2)}$ depends on $\chi^{(1)}$. Hence, the equations must be iterated to self-consistency. As with our fourth-order perturbation theory, the computational effort will be similar to that of CISDTQ or CCSDTQ treatments in molecular physics.

5. Application to coupled, anisotropic anharmonic oscillators

In tables 1 and 2, we present the results of calculations using our QDPT for two representative sets of parameters. Table 2 also includes QDCC results; QDCC results were omitted from table 1 as they were virtually indistinguishable from the exact values. "Exact" values were obtained from variational calculations sufficiently large such that increases in the basis set size no longer changed any reported digits. The first results columns of the tables report the energy correct through first order; i.e., diagonalization of the full Hamiltonian within the basis defining the quasidegenerate level. Comparison of the exact results with the first-order values gives the contribution to the total energy which originates from outside the quasidegenerate level and, so, is the true test of the perturbation method. Results for second- and fourth-order quasidegenerate perturbation theory and quasidegenerate coupled cluster theory are given as deviations from the exact result. For example, the QDPT2 result for the second root of the second level in table 1 is $E(\text{QDPT2}) = 2.237\,466 - 5.9 \times 10^{-5} = 2.237\,407$.

Table 1
Errors in calculated energies for $\gamma = 0.1, a/k = 0.1, b/(k\beta^2) = 0.05$.

Level	Root	E^1	Exact	δQDPT2	δQDPT4
0	0	1.030992	1.026684	3.5 (−5)	1. (−6)
1	0	1.923376	1.918181	5.3 (−5)	1. (−6)
	1	2.262574	2.237466	−5.9 (−5)	9. (−6)
2	0	2.815813	2.809749	7.0 (−5)	2. (−6)
	1	3.158980	3.133127	−6.3 (−5)	1.0 (−5)
	2	3.614050	3.533270	−1.8 (−3)	1.4 (−4)
3	0	3.708300	3.701387	8.6 (−5)	3. (−6)
	1	4.055362	4.028756	−6.4 (−5)	1.1 (−5)
	2	4.512011	4.430401	−1.9 (−3)	1.5 (−4)
	3	5.087963	4.902882	−1.3 (−2)	1.9 (−3)
4	0	4.600836	4.593092	1.0 (−4)	3. (−6)
	1	4.951723	4.924356	−6.2 (−5)	1.1 (−5)
	2	5.409959	5.327517	−2.0 (−3)	1.6 (−4)
	3	5.986656	5.800718	−1.3 (−2)	2.0 (−3)
	4	6.685124	6.337723	−5.9 (−2)	1.7 (−2)

Table 2
Errors in calculated energies for $\gamma = 0.1, a/k = 0.2, b/(k\beta^2) = 0.2$.

Level	Root	E^1	Exact	δQDPT2	δQDPT4	δQDCC
0	0	1.123 967	1.086 936	6.3 (−4)	1.2 (−4)	5. (−6)
1	0	2.009 742	1.968 637	9.9 (−4)	1.7 (−4)	9. (−6)
	1	2.734 060	2.512 909	−1.1 (−2)	1.8 (−3)	8.2 (−5)
2	0	2.895 658	2.850 645	1.3 (−3)	2.2 (−4)	1.6 (−5)
	1	3.631 280	3.407 259	−1.1 (−2)	2.0 (−3)	8.2 (−5)
	2	4.828 433	4.150 709	−1.3 (−1)	5.1 (−2)	5.7 (−4)
3	0	3.781 709	3.732 940	1.7 (−3)	2.8 (−4)	2.4 (−5)
	1	4.528 396	4.301 396	−1.2 (−2)	2.3 (−3)	7.9 (−5)
	2	5.727 352	5.046 982	−1.2 (−1)	5.3 (−2)	5.5 (−4)
	3	7.417 088	5.950 672	–	–	−7.6 (−5)
4	0	4.667 889	4.615 502	2.0 (−3)	3.4 (−4)	3.3 (−5)
	1	5.425 414	5.195 337	−1.2 (−2)	2.5 (−3)	7.4 (−5)
	2	6.626 251	5.943 216	−1.2 (−1)	5.6 (−2)	5.2 (−4)
	3	8.316 512	6.847 779	–	–	−2.4 (−4)
	4	10.501 125	7.884 618	–	–	−2.4 (−2)

All calculations reported in table 1 were performed with the full quasidegenerate space; i.e., the dimension of the buffer space was zero. The larger intruder state problem in the calculations reported in table 2 required the use of a nonzero buffer space for quasidegenerate level 3 and above. Table 2 supports the hypothesis that our implementation of intermediate Hamiltonians can obtain accurate eigenvalues for some states even when perturbation theory fails for states too close to the intruder states. The quasidegenerate coupled cluster calculations were seen to converge even for states that were required to be in the buffer space in perturbation theory calculations.

We performed further analyses of data presented in tables 1 and 2 in order to understand better the effect of increasing energy eigenvalues. Table 3 presents percentage error of data from table 1; likewise, table 4 presents further analyses of data from table 2. For all perturbation theory results, we see a gradual deterioration in accuracy within each quasidegenerate level, but essentially no change in relative accuracy of corresponding roots between levels. For example, using the QDPT4 results, the second root of level 1 is in error by 0.81%; the errors of the second root of levels 2, 3, and 4 are 0.89%, 1.0%, and 1.1%, respectively. The coupled cluster results are similar, except for levels in which intruder states forced the use of a buffer space with the perturbation theory; in those levels, the QDCC results, while still accurate, had less systematic errors.

Table 3
Percent errors in calculated energies for $\gamma = 0.1, a/k = 0.1, b/(k\beta^2) = 0.05$.

Level	Root	ΔE	% error (QDPT2)	% error (QDPT4)
0	0	0.037 031	0.81	0.023
1	0	0.005 195	1.0	0.019
	1	0.025 108	0.23	0.036
2	0	0.006 064	1.2	0.033
	1	0.025 853	0.24	0.039
	2	0.080 780	2.2	0.17
3	0	0.006 913	1.2	0.043
	1	0.026 606	0.24	0.041
	2	0.081 610	2.3	0.18
	3	0.185 081	7.0	1.0
4	0	0.007 744	1.3	0.039
	1	0.027 367	0.23	0.040
	2	0.082 442	2.4	0.19
	3	0.185 938	7.0	1.1
	4	0.347 401	17.	4.9

Table 4
Percent errors in calculated energies for $\gamma = 0.1, a/k = 0.2, b/(k\beta^2) = 0.2$.

Level	Root	ΔE	% error (QDPT2)	% error (QDPT4)	% error (QDCC)
0	0	0.037 031	1.7	0.32	0.014
1	0	0.041 105	2.4	0.41	0.022
	1	0.221 151	5.0	0.81	0.037
2	0	0.045 013	2.9	0.49	0.036
	1	0.224 021	4.9	0.89	0.037
	2	0.677 724	19.	7.5	0.084
3	0	0.048 769	3.5	0.57	0.049
	1	0.227 000	5.3	1.0	0.035
	2	0.680 370	18.	7.8	0.081
	3	1.466 416	–	–	0.0051
4	0	0.052 387	3.8	0.65	0.063
	1	0.230 077	5.2	1.1	0.032
	2	0.683 035	18.	8.2	0.076
	3	1.468 733	–	–	0.016
	4	2.616 507	–	–	2.4

6. Summary

A partitioning of the Hamiltonian by number of mappings from a subspace of interest has been introduced in a canonical Rayleigh-Schrödinger quasidegenerate perturbation theory. Tractable equations through fourth order have been explicitly presented. An intermediate Hamiltonian, based on a double perturbation, was introduced to screen especially problematic states of the subspace of interest. Numerical studies on coupled anisotropic anharmonic oscillators have shown high accuracy, even in the presence of small eigenvalue splittings between the subspace of interest and the adjoining region. A quasidegenerate coupled cluster method based on an intermediate normalization quasidegenerate perturbation theory was introduced and shown to give excellent results when perturbation series were convergent and useful results even in the presence of true intruder states.

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