Self-consistent field perturbation theory of molecular vibrations

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Perturbation theory is used to perform non-iterative calculations of energy eigenvalues of the coupled ordinary differential equations that result from imposing separability assumptions in terms of normal coordinates on vibrational wavefunctions. Various model Hamiltonians with 2 or 3 coupled normal modes are studied and the increase of computational cost with the number of degrees of freedom is analysed. Quadratic Padé approximants of the perturbation expansions are rapidly convergent, and directly yield complex numbers for resonance eigenvalues. For a 3-mode system, results are obtained within partial separability assumptions, with a pair of modes left coupled. Large-order perturbation theory with partial separability is suggested as an alternative to low-order exact perturbation theory.

1. Introduction

The vibrational self-consistent field (VSCF) approximation [1–3], in which the molecular vibrational wavefunction is expressed as a separable product of normal-coordinate functions, extends normal-mode analysis to mildly coupled systems with only a modest increase in computational difficulty. For tightly bound molecules such as H_2O and CO_2 the separability assumption introduces a systematic error in the energy of the order of 1%. However, it makes the analysis of large systems computationally feasible [4–6]. To improve the accuracy, VSCF wavefunctions can be used as the basis for a 'state-interaction' calculation, analogous to the configuration–interaction method for electronic structure calculations, but this greatly increases the computational cost.

Here we study VSCF approximations in the context of large-order perturbation theory. It was demonstrated recently that large-order Rayleigh–Schrödinger perturbation theory can have a significant advantage in computational cost over variational methods for solving the Schrödinger equation for vibration spectra [7] and vibration–rotation spectra [8]. In addition, it is a convenient approach for calculating resonance energies, because the computational algorithm for resonance eigenvalues is equivalent to that for bound states, as long as appropriate summation approximants are used [9–11].

In [12] a general algorithm was developed for solving SCF equations with perturbation theory. Perturbation theory decouples the equations order by order, thus yielding direct non-iterative solutions for asymptotic expansions of wavefunctions and energies. Furthermore, it was shown that perturbation theory was straightforward to apply with partial separability, with the wavefunction expressed as a separable product of functions that depend on clusters of normal coordinates.

We have several motivations for developing an SCF perturbation theory of molecular vibrations. The first is to provide a feasible strategy for applying perturbation theory to large molecules. The cost of computing high-order coefficients of perturbation expansions increases rapidly with the number of degrees of freedom. Large-order SCF perturbation theory is an alternative to low-order exact perturbation theory. Thus one can eliminate the error from premature truncation of the expansion at the cost of introducing a systematic error from a separability assumption. Another motivation is to study the accuracy of partial separability assumptions. Partial separability offers an alternative to the state-interaction method for systematically improving the accuracy of VSCF calculations. It can also be used as a probe of the degree of interaction between particular normal modes. Finally, SCF perturbation theory can be applied to a wide variety of problems including, for example, the electronic Schrödinger equation [12–14]. The molecular vibration problem is a straightforward test case for the general theory.

In section 2 we outline the calculation method. In section 3 we briefly treat a special case in which the SCF equations can be solved exactly, and then present results from perturbation theory for various 2- and 3-mode systems that have been treated previously in the literature. The emphasis is on determining the rate of

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convergence of the perturbation expansions and on studying the accuracy of the SCF approximation for imaginary parts of resonance energies. For a 3-mode system we compare the accuracy of partial separability approximations to that of state-interaction calculations. Section 4 contains an analysis of how the computational cost of large-order SCF perturbation theory increases with the number of degrees of freedom. In section 5 we discuss potential advantages of this theory and suggest future applications.

2.   SCF theory

Consider a Hamiltonian of the form

$$H = w(\mathbf{q}) + \sum_{\alpha=1}^{N} h^{(\alpha)}(q_\alpha), \qquad (1)$$

where

$$h^{(\alpha)} = -\frac{1}{2}\frac{\partial^2}{\partial q_\alpha^2} + \frac{1}{2}\omega_\alpha^2 q_\alpha^2 + \eta_{\alpha,1}q_\alpha^3 + \eta_{\alpha,2}q_\alpha^4 + \cdots. \quad (2)$$

$\mathbf{q} = \{q_1, q_2, \ldots, q_N\}$ is the set of harmonic normal coordinates, which diagonalizes the harmonic expansion of H, and $w(\mathbf{q})$ is a polynomial with degree of at least 3 that couples the q_α. This type of Hamiltonian could arise from the use of a finite-degree polynomial fit to *ab initio* or empirical information for the potential energy operator or from the use of a Taylor expansion of an analytical potential function. The SCF method consists of replacing the partial differential Schrödinger equation $H\Psi = E\Psi$ with a set of coupled ordinary differential equations,

$$(H^{(\alpha)} - \varepsilon^{(\alpha)})\psi^{(\alpha)}(q_\alpha) = 0, \qquad (3a)$$

$$H^{(\alpha)} = h^{(\alpha)}(q_\alpha) + \bar{w}^{(\alpha)}(q_\alpha), \qquad (3b)$$

$$\bar{w}^{(\alpha)}(q_\alpha) = \left\langle \prod_{\beta\neq\alpha}\psi^{(\beta)}(q_\beta) \middle| w(\mathbf{q}) \middle| \prod_{\beta'\neq\alpha}\psi^{(\beta')}(q_{\beta'}) \right\rangle \qquad (3c)$$

Equation (3) results from substituting for the wavefunction a separable product $\Psi = \prod_\alpha \psi^{(\alpha)}(q_\alpha)$ and then applying the variational principle for the energy with Ψ constrained to be normalized.

Let

$$H = \sum_{\alpha=1}^{N}\left(-\frac{1}{2}\frac{\partial^2}{\partial q_\alpha^2} + \frac{1}{2}\omega_\alpha^2 q_\alpha^2\right) + H', \qquad (4)$$

where H' is the sum of w and all of the anharmonic terms in the $h^{(\alpha)}$. We will write H' in the form

$$H' = \sum_{k=1}^{}\kappa^{k/2}\left[w_k(\mathbf{q}) + \sum_\alpha\eta_{\alpha,k}q_\alpha^{k+2}\right], \qquad (5)$$

where κ is a perturbation parameter and the w_k are sums

of monomials of degree $k + 2$ that couple normal coordinates. The physical solution corresponds to $\kappa = 1$. It follows that $\psi^{(\alpha)}$ and the $\varepsilon^{(\alpha)}$ have asymptotic expansions

$$\psi^{(\alpha)}(q_\alpha) = \sum_{k=0}^{\infty}\kappa^{k/2}\psi_k^{(\alpha)}(q_\alpha), \qquad (6)$$

$$\varepsilon^{(\alpha)} = \sum_{k=0}^{\infty}\kappa^{k/2}\varepsilon_k^{(\alpha)}. \qquad (7)$$

Substituting these into equation (3) and collecting terms multiplied by $\kappa^{k/2}$ yields a set of N equations for each value of k. These equations are coupled implicitly through the dependence of $\bar{w}^{(\alpha)}$ on the $\psi^{(\beta\neq\alpha)}$. The total vibrational energy is

$$E = \frac{1}{N}\sum_\alpha\varepsilon^{(\alpha)} + \frac{N-1}{N}\sum_\alpha\langle h^{(\alpha)}\rangle$$

$$+ \frac{N-2}{N}\sum_{\alpha_1<\alpha_2}\langle w^{(\alpha_1,\alpha_2)}\rangle + \cdots$$

$$+ \frac{1}{N}\sum_{\alpha_1<\alpha_2<\cdots<\alpha_{N-1}}\langle w^{(\alpha_1,\alpha_2,\ldots,\alpha_{N-1})}\rangle, \qquad (8)$$

where the $w^{(\alpha_1,\ldots)}$ are the terms in $w(\mathbf{q})$ that couple the designated normal coordinates. Here we will consider only functions H' such that $H'(-\mathbf{q}, \kappa^{1/2}) = H'(\mathbf{q}, -\kappa^{1/2})$. It follows that the asymptotic expansion of E will include only integer powers of κ.

Now consider the expansions in powers of $\kappa^{1/2}$ that result for the terms $\bar{w}^{(\alpha)}(q_\alpha)$. Substituting equation (6) into (3c) yields a sum of terms $\langle\psi_{k_1}^{(\beta)}|w_{k_2}|\psi_{k_3}^{(\beta)}\rangle$. For terms at order $\kappa^{k/2}$ we have $k_1 + k_2 + k_3 = k$. However, the smallest possible value of k_2 is 1, which implies that the largest possible value for k_1 or k_3 is $k - 1$. Therefore, the equation that determines $\psi_k^{(\alpha)}$ depends on the $\psi_{k'}^{(\beta\neq\alpha)}$ only for $k' < k$. Thus, perturbation theory uncouples the SCF equations order by order. Detailed derivations of the perturbation equations, and an efficient linear algebraic algorithm for solving them, are given in [12]

It is straightforward to extend this method to cases in which w contains differential operators and to cases in which the wavefunctions are subject to less drastic separability assumptions [12] for example,

$$\Psi(\mathbf{q}) = \psi^{(a)}(\mathbf{q}_a)\psi^{(b)}(\mathbf{q}_b)\psi^{(c)}(\mathbf{q}_c)\cdots, \qquad (9)$$

where the $\mathbf{q}_\alpha$ are arbitrary subsets of the full set $\mathbf{q}$.

3.   Results
3.1. *An exactly solvable case*

Consider a system of two harmonic oscillators with

cubic coupling, described by the Hamiltonian

$$H = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\omega_x^2 x^2 + \frac{1}{2}\omega_y^2 y^2 - \lambda x y^2, \quad (10)$$

which has been used widely to model the vibrations of non-bending triatomic molecules [15] The mode-averaged Hamiltonians are

$$H^{(x)} = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{1}{2}\omega_x^2 x^2 - \lambda\langle y^2\rangle x, \quad (11\,a)$$

$$H^{(y)} = -\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\bar{\omega}_y^2 y^2, \quad (11\,b)$$

where $\bar{\omega}_y^2 = \omega_y^2 - 2\lambda\langle x\rangle$. The change of variable

$$x = \tilde{x} + \langle x\rangle = \tilde{x} + \lambda\langle y^2\rangle/\omega_x^2 \quad (12)$$

yields a system of unperturbed harmonic oscillators, with total energy

$$E = (n_x + \tfrac{1}{2})\omega_x + (n_y + \tfrac{1}{2})\bar{\omega}_y + (n_y + \tfrac{1}{2})^2\frac{\lambda^2}{2\omega_x^2\bar{\omega}_y^2}, \quad (13)$$

where $\bar{\omega}_y$ is determined from the equation

$$\bar{\omega}_y^3 - \omega_y^2\bar{\omega}_y + (2n_y + 1)\lambda^2/\omega_x^2 = 0. \quad (14)$$

The SCF energy is complex if

$$\lambda^2 > \frac{\sqrt{3}}{9}(n_y + \tfrac{1}{2})^{-1}\omega_x^2\omega_y^3, \quad (15)$$

in which case the eigenstate represents a resonance. The energy of the resonance is $\Re E$ and the width is $\Gamma \approx 2|\Im E|$ [16] Since the value of the last term in equation (13) does not depend on n_x, the width of the resonance, within the SCF approximation, depends only on n_y. Figure 1 compares the SCF results to exact results for various eigenstates. (The 'exact' energies were calculated with large-order perturbation theory [7] without the separability assumption.) We have subtracted $(n_x + \tfrac{1}{2})\omega_x$ from the real part in figure 1 to make the SCF curves independent of n_x. The exact results show a weak dependence on n_x. The exact imaginary part is nonzero for all $\lambda > 0$, although it becomes exponentially small as λ approaches zero.

Note that the accuracy of the SCF approximation for the state $(n_x, n_y) = (0, 1)$ is greater than that for $(1, 0)$. This is perhaps due to the fact that equation (13) includes nonlinear behaviour only in n_y; the n_x spectrum within the SCF approximation is purely harmonic. We find that the SCF results for the $(0, n)$ states in general tend to be more accurate than those for the $(n, 0)$ states, although this trend becomes less noticeable for very large n.
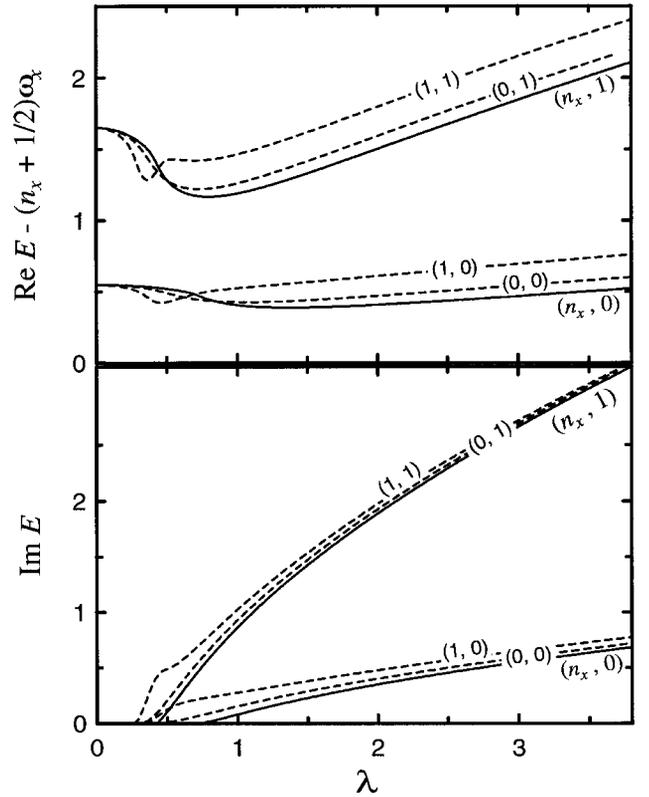

Figure 1. Real and imaginary parts of the energy eigenvalues of the Hamiltonian in equation (10) with $\omega_x = 1$ and $\omega_y = 1.1$, versus the coupling constant λ. Solid curves show SCF results while the dashed curves show exact results. The curves are labelled by the quantum numbers (n_x, n_y). The SCF results are independent of n_x.

3.2. *2-mode systems*

Consider the Hamiltonian

$$H = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\omega_x^2 x^2 + \frac{1}{2}\omega_y^2 y^2 - \lambda(xy^2 + \eta x^3), \quad (16)$$

which was studied by Eastes and Marcus [17] for various values of ω_x, ω_y, λ and η Let $\kappa^{1/2} = \lambda$ be the perturbation parameter. Expansions for the exact energy eigenvalues, without separability, were calculated in [7] Although these expansions are in principle divergent if taken to high enough order [18] in practice the partial sums were rapidly convergent and the rate of convergence could be increased by Padé summation. We find that the SCF expansions behave similarly, but the rate of convergence is even more rapid than for the exact perturbation expansions. Furthermore, we find that the convergence for both the exact and the SCF expansions can be improved by using quadratic Padé
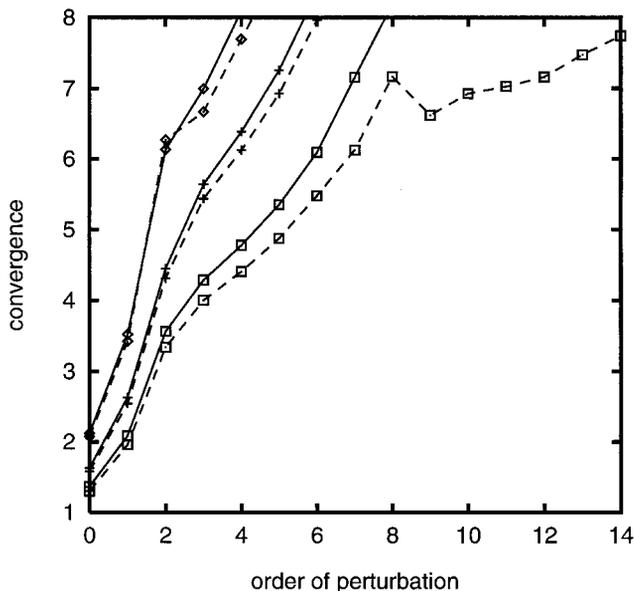
Figure 2. Convergence of quadratic Padé approximants for SCF energies (solid curves) and exact energies (dashed curves) for the 2-mode cubic oscillator with Hamiltonian given by equation (16) with $\omega_x = 0.541\,98$, $\omega_y = 1.458\,02$, $\lambda = 0.111\,60$, $\eta = 0.084\,14$. The ordinate is $-\log_{10}\left|(E_{approx} - E_\infty)/E_\infty\right|$, where E_{approx} is the result from the summation approximant at given order and E_∞ is the converged result from large-order perturbation theory. Diamonds indicate the $(n_x, n_y) = (0, 0)$ state, crosses the $(2, 0)$ state, and squares the $(2, 2)$ state.

approximants [19],

$$S_{[n,m,l]} = \frac{1}{2R_n}\left(Q_m \pm \left[Q_m^2 + 4P_l R_n\right]^{1/2}\right), \quad (17)$$

where P_l, Q_m, and R_n are polynomial of degrees l, m, n, respectively, in the expansion parameter. These polynomials are determined from the asymptotic relation

$$RE^2 + QE - P = O(\kappa^{n+m+l+2}), \quad (18)$$

with E in equation (18) representing the asymptotic expansion of the energy. A comparison of the convergence of the quadratic approximants for the exact and SCF expansions is given in figure 2.

Quadratic approximants are especially useful for resonance eigenvalues [9–11]. Since the expansion coefficients that we calculate for E are real numbers, the standard linear Padé approximants $S_{[n,m]} = P_n/Q_m$, defined by $QE - P = O(\kappa^{n+m+1})$, will always be real. However, quadratic approximants will give an imaginary part when the discriminant is negative. Figure 3 compares the converged values of SCF and exact energies. The qualitative trends in the accuracy of the SCF approximation are similar to those in figure 1.
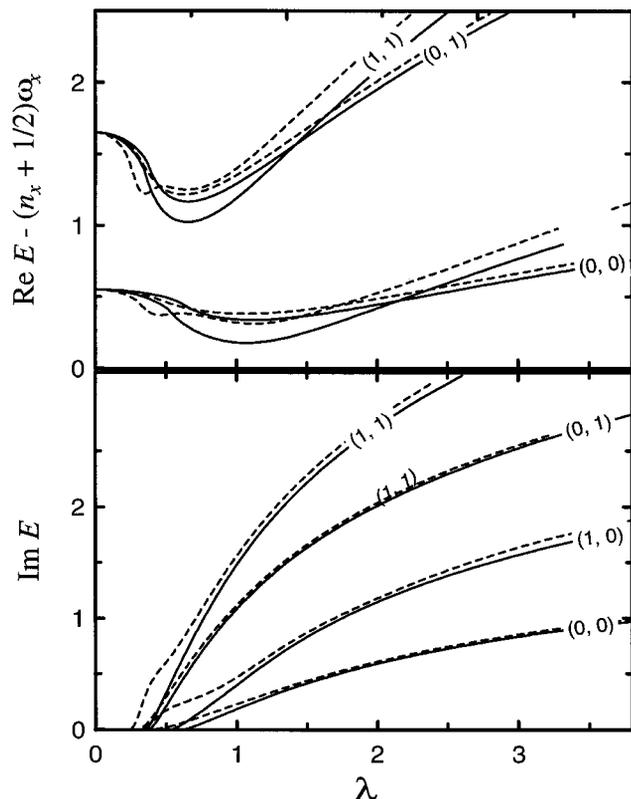

Figure 3. Real and imaginary parts of the energy eigenvalues of the Hamiltonian in equation (16), with $\omega_x = 1$, $\omega_y = 1.1$ and $\eta = 0.1$, versus the coupling constant λ. Solid curves show SCF results while the dashed curves show exact results. The curves are labelled by the quantum numbers (n_x, n_y).

Another model for vibrational resonances is

$$H = -\frac{1}{8}\frac{\partial^2}{\partial x^2} - \frac{1}{8}\frac{\partial^2}{\partial y^2} + V(x, y), \quad (19a)$$

$$V(x, y) = \frac{1}{2}\omega_x^2 x^2 e^{-x^2} + \frac{1}{2}\omega_y y^2 - \frac{1}{2}\omega_y^2 x^2 y^2 e^{-x^2}, \quad (19b)$$

which was devised by Waite and Miller [20] to describe unimolecular dissociation, and has been studied within the SCF approximation by Christoffel and Bowman [21] and by Farrelly and coworkers [22, 23]. The potential has a symmetric double barrier in the x mode. It is convenient to express this problem as a semiclassical perturbation theory [24], with the perturbation parameter multiplying the kinetic energy:

$$\left[\kappa^2\left(-\frac{1}{8}\frac{\partial^2}{\partial x^2} - \frac{1}{8}\frac{\partial^2}{\partial y^2}\right) + V(x, y) - E\right]\Psi = 0. \quad (20)$$

If we make the substitutions $x \to \kappa^{1/2}x$, $y \to \kappa^{1/2}y$, and $E \to \kappa E$ and then expand the potential in powers of $\kappa^{1/2}$, then we obtain a Hamiltonian that is essentially in the form given by equations (4) and (5). SCF results
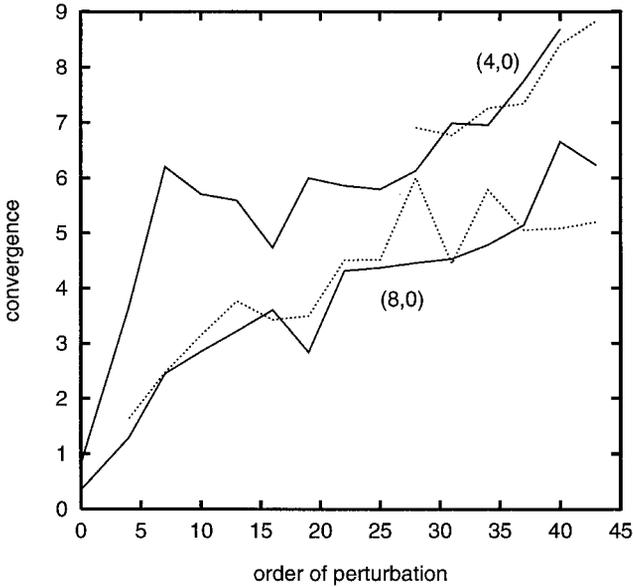
Figure 4. Convergence of quadratic Padé approximants for SCF energies from the Hamiltonian given by equation (19) with quantum numbers $(n_x, n_y) = (4, 0)$ and $(8, 0)$. Solid curves correspond to $-\log_{10}|(\Re E_{approx} - \Re E_\infty)/\Re E_\infty|$ and dotted curves to $-\log_{10}|(\Im E_{approx} - \Im E_\infty)/\Re E_\infty|$, where E_∞ is the 49th-order result and E_{approx} is the value of the diagonal quadratic approximant at given order.

Table 1. Energy eigenvalues of the Hamiltonian given by equation (19). Results from SCF perturbation theory (49th-order, summed with quadratic approximants) are compared with results of iterative complex-coordinate SCF theory from numerical integration. The barrier height is 36.777 in the uncoupled x-coordinate potential.

n_x	n_y	SCFPT	Iterative SCF[a]
4	0	30.673 282 1 – i0.000 045 7	30.675 – i0.441 × 10⁻⁴
4	1	37.126 394 8 – i0.000 088 7	
5	0	35.209 647 – i0.006 208	35.212 – i0.594 × 10⁻²
6	0	38.802 13 – i0.187 43	38.805 – i0.185
8	0	43.884 2 – i3.163 5	43.885 – i3.162

[a] Reference [23].

from quadratic Padé summation are presented in table 1. Figure 4 shows representative convergence plots. The accuracy obtained at given order for the imaginary part is approximately the same as that for the real part.

3.3. *A 3-mode system*

Consider the Hamiltonian

$$H = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} - \frac{1}{2}\frac{\partial^2}{\partial z^2}$$
$$+ \tfrac{1}{2}\omega_x^2 x^2 + \tfrac{1}{2}\omega_y^2 y^2 + \tfrac{1}{2}\omega_z^2 z^2$$
$$- \kappa^{1/2}(xy^2 + yz^2 + \eta x^3 + \eta y^3), \quad (21)$$

with $\omega_x = 0.7$, $\omega_y = 1.3$, $\omega_z = 1.0$, $\eta = 0.1$, and $\kappa^{1/2} = 0.1$. This is another standard test case [25–27]. There are now four possible normal-mode separability assumptions: three in which a pair of modes is left coupled and one with all modes separated.

Christoffel and Bowman [26] used an iterative method to calculate SCF energies for this system and then used an expansion of the exact wavefunction in terms of a finite set of SCF wavefunctions to obtain a variational estimate for the exact energy. This 'state-interaction' method will converge to the exact energy (for bound states) as the size of the SCF basis is increased. The computational cost is not too high for 3-mode systems, but increases rapidly with the number of degrees of freedom. Norris *et al.* recently studied this system using Møller–Plesset perturbation theory [27].

We consider the cases $\Psi_{\{x;y,z\}} = \psi^{(a)}(x)\psi^{(b)}(y,z)$ and $\Psi_{\{z;x,y\}} = \psi^{(a)}(x,y)\psi^{(b)}(z)$. (The case $\{y; x, z\}$ is for this system equivalent to full separability, since none of the coupling terms in equation (21) couples x and z.) Figure 5 compares the accuracy of the various separability assumptions for the states $(n_x, 0, 0)$ and $(0, n_y, 0)$. As n_x increases, the accuracy of $\{z; x, y\}$ holds steady while $\{x; y, z\}$ and $\{x; y; z\}$ become less accurate. Increasing n_x causes an increase in the expectation value of $|x|$, which increases the importance of the term xy^2 in equation (21); hence, the approximations with x and y separated become less accurate as this term becomes more important. As n_y increases, the $\{x; y, z\}$ separability approximation becomes the most accurate. This appears to be analogous to the trend seen in figure 1 for the exactly solvable problem. If the coupling between two normal coordinates has the form $q_1 q_2^2$, then the SCF approximation tends to be more accurate for $(0, n_2)$ excitations than for $(n_1, 0)$ excitations. Thus, $\{x; y, z\}$ separability with xy^2 coupling and n_y excitation tends to be more accurate than $\{z; x, y\}$ with yz^2 coupling and n_y excitation.

Also shown in figure 5 is the accuracy obtained using the state-interaction method, with various basis sizes, for those cases in which the results in [26] are of sufficient precision for comparison. For the $(2, 0, 0)$ state the $\{z; x, y\}$ approximation is comparable in accuracy to a state-interaction calculation with a 39-state basis set consisting of all states with $n_x + n_y + n_z < 5$. For the $(1, 0, 0)$ state it is less accurate than a 39-state calculation but more accurate than a 20-state calculation $(n_x + n_y + n_z < 4)$. For the ground state it is less accurate than a 20-state calculation but more accurate than a 10-state calculation $(n_x + n_y + n_z < 3)$. For $(0, 1, 0)$ the
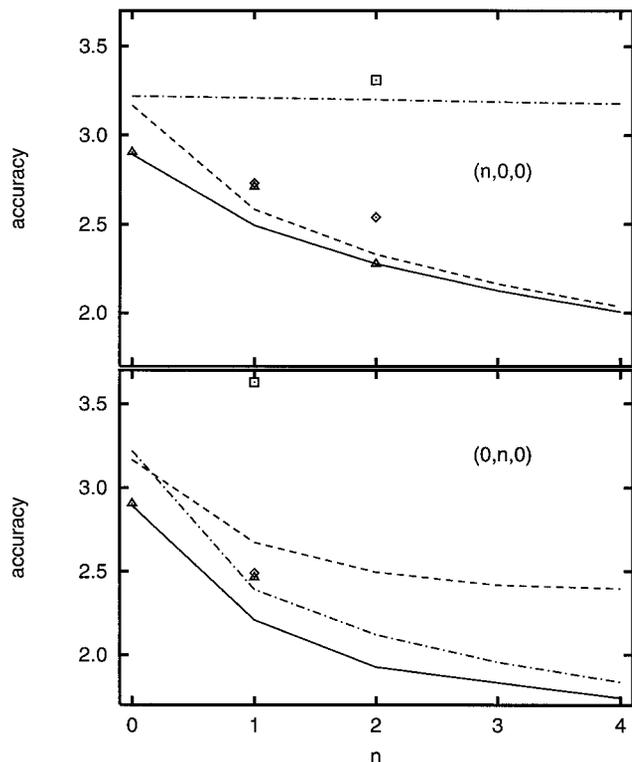
Figure 5. Accuracy versus quantum number from the various SCF approximations for the 3-mode system described by equation (21), with accuracy defined as $-\log_{10}|E_{SCF} - E_{exact}|$ with E in atomic units. E_{exact} is the converged result from exact large-order perturbation theory. E_{SCF} is from perturbation theory with the following separability assumptions: $\{x; y, z\}$ [dashed curves], $\{z; x, y\}$ [dash-dotted curves], $\{x; y; z\}$ [solid curves]. The quantum numbers (n_x, n_y, n_z) are as indicated. Also shown are results of state-interaction calculations from [26] for basis set size 10 ($\triangle$), 20 ($\diamond$), and 39 ($\square$).

$\{x; y, z\}$ approximation is between the 20- and 39-state calculations in accuracy.

4. Computational cost

One advantage of SCF perturbation theory over exact perturbation theory is a decrease in computer memory requirements. Consider a system with N degrees of freedom. For exact perturbation theory the wavefunction component Ψ_k at order k in the expansion can be described [28] by a tensor $\mathbf{a}_k$ of rank N that contains the coefficients of a linear superposition of harmonic eigenfunctions. In each dimension of the tensor the number of nonzero elements increases linearly with k. Therefore the SCF approximation reduces the scaling with k from k^N to $\sum_{\alpha} k^{N_\alpha}$ where N_α is the number of coupled coordinates in coordinate group α.

Another advantage of SCF approximations is a decrease in computational time; that is, the number of arithmetic operations needed to compute the energy ex-

pansion to given asymptotic order. Consider the computational cost of exact (unseparated) perturbation theory. The recursion relation [7, 28] that expresses the tensor $\mathbf{a}_j$ in terms of the $\mathbf{a}_{i<j}$ has the following form for harmonic Hamiltonians with polynomial perturbations:

$$\mathbf{a}_j = \mathbf{K}\left(\mathbf{V}\mathbf{a}_{j-1} + \sum_{i=1}^{j} \varepsilon_i \mathbf{a}_{j-i} \right). \tag{22}$$

$\mathbf{K}$ is a diagonal operator that depends on the frequencies and quantum numbers, $\mathbf{V}$ is the operator representation of the perturbing potential, and the ε_j are the energy expansion coefficients. The ε_j are given by the equation $\varepsilon_j \mathbf{a}_0 = \mathbf{V}\mathbf{a}_{j-1}$. Explicit expressions for $\mathbf{K}$ and $\mathbf{V}$ for various oscillator systems are given in [7] and [30]. In the limit of large j the number of arithmetic operations in equation (22) is proportional to j^{N+1}, due to the summation over i. Therefore, a calculation of the perturbation theory through order k has a cost proportional to k^{N+2}.

The SCF approximations reduce the cost from the recursion relations to $\sum_{\alpha} k^{N_\alpha+2}$ in the limit of large k. However, they replace the term $\mathbf{V}\mathbf{a}_{j-1}$ with a sum in the form $\sum_{i=1}^{j} \mathbf{V}_i \mathbf{a}_{j-i}$. Additional operations are needed to compute the operators $\mathbf{V}_i$, which for a given coordinate group depend on the wavefunction tensors of the other coordinate groups, and to calculate the $\mathbf{V}_i \mathbf{a}_{j-i}$. These new operations do not increase the exponents in the cost scaling but they do increase the proportionality constant. For a high enough order the SCF calculation will have a cost advantage over the exact calculations, but this may not always be the case for lower orders. In general, for an arbitrary number of degrees of freedom, the greatest cost savings will be obtained when the coordinates are divided into groups that are approximately equal in size.

A third advantage of the SCF approximations is an improvement in the rate of convergence of the perturbation expansions, which was illustrated in figure 2. This effect appears to increase with the degree of excitation.

5. Discussion

SCF perturbation theory extends the applicability of exact perturbation methods in the same way that iterative SCF theory does for the standard variational treatment, in which the Hamiltonian is diagonalized in a finite basis. Results from various studies [7, 8, 10, 12, 18, 27, 29–32] suggest that perturbation theory has potentially significant advantages over diagonalization: It can be more cost efficient, it provides a flexible theoretical framework for formulating new approximation schemes, and it gives a uniform approach to different types of calculation.

A clear advantage in cost efficiency of perturbation theory over diagonalization for calculating vibrational

spectra (without separability assumptions) was demonstrated in [7]. For vibration–rotation spectra the advantage can be even more significant, using a semiclassical perturbation theory [8, 30]. For VSCF calculations with full separability this cost advantage is not so important, since standard methods are extremely efficient [4, 6]. However, in treatments of large molecules using partial separability with large cluster sizes the advantage of perturbation theory over diagonalization could be significant.

The flexibility of perturbation theory is exemplified by our VSCF calculations with partial separability. Perturbation theory is a natural technique for this calculation since only minor modifications of the computational algorithm are required in order to invoke separability in terms of clusters of coordinates instead of individual coordinates. This approach is not limited to the use of normal coordinates. It is possible to extend the method to treat separability assumptions in terms of arbitrary coordinates. This is important, since it is well known that the accuracy of VSCF approximations can depend strongly on the choice of coordinates [33, 34].

The uniform nature of perturbation theory is illustrated by the fact that our treatment of resonances is identical to that for bound states. This makes the method well suited to the study of states with energies close to the classical dissociation energy, which would be important, for example, in an *ab initio* treatment of unimolecular reaction rates. Furthermore, the computational algorithm used here can describe the dynamics of electrons as well as that of nuclei. For example, in [14] we used a semiclassical SCF perturbation expansion to solve the electronic Schrödinger equation for a hydrogen atom in a strong magnetic field and in [13] first-order SCF dimensional expansions were used to study electron correlation in two-electron atoms.

Partial separability assumptions offer a compromise between the computationally efficient but somewhat inaccurate limit of full separability and the less efficient but exact state-interaction method. This approach is related closely to the dressed-state truncation–recoupling theory proposed by Bowman and Gazdy [35], in which a subset of modes is left coupled while the remaining 'dressing' modes are treated as completely separable. The most efficient application of VSCF perturbation theory is for calculations with the modes evenly partitioned into clusters.

It is of particular interest to compare *low*-order perturbation theory of the non-separated exact problem to our *large*-order theory with partial separability. The former method introduces a truncation error while the latter method sums the perturbation expansion with high precision but at the cost of a systematic error from the separability assumption. An advantage of the low-order exact theory is that it is easier to implement. The computational algorithms for exact perturbation theories [7, 28–30] are simpler than that for SCF theory. If the anharmonic terms in the potential are not too large then the convergence of the perturbation expansion can be sufficiently fast that the truncation error will be smaller than the SCF error, but if there is strong anharmonicity and weak coupling then the truncation can cause the larger error. For example, with the Hamiltonian of equation (21) exact Rayleigh–Schrödinger perturbation theory for the ground state at first order is already more accurate than the converged SCF results. However, if the anharmonicity constant η is increased by a factor of 5, then it is not until order 9 that the truncation error becomes smaller than the $\{z; x, y\}$ SCF error. Of course, if there is a clear physical reason for partitioning the coordinates, then partial separability will be relatively more accurate. For example, if the xy^2 coupling constant in equation (21) is increased by a factor of 5, then the exact theory again does not surpass the converged $\{z; x, y\}$ accuracy until order 9. Finally, an appealing feature of SCF theory is that the error it introduces has a much more straightforward physical interpretation (i.e., separable dynamics) than does the error from low-order truncation of an exact theory. By determining the accuracies of different separability assumptions one could hope to develop a qualitative understanding of the complicated dynamics of polyatomic molecular vibration.

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