

# Møller–Plesset perturbation theory applied to vibrational problems

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Møller–Plesset perturbation theory is employed to improve the accuracy of static mean field computations in molecular vibration problems. This method is a simple and efficient way to get nearly exact frequencies for few-mode model potentials. For more realistic potentials representing the dynamics of water and formaldehyde, the Møller–Plesset treatment works equally as well. However, we find in general that MP2 level corrections give very accurate energies and additional corrections by higher level terms in the MP series are not substantial. Moreover, we find that for reference states on high energy manifolds degeneracies can result when higher level terms are included in the series. We discuss several ways to remove these degeneracies. © 1996 American Institute of Physics. [S0021-9606(96)03947-5]

## I. INTRODUCTION

Interest in the twin problems of accurate vibrational spectroscopy and intramolecular vibrational relaxation, coupled with the ability of electronic structure techniques to produce accurate potential energy surfaces, has resulted in a number of improved methods for finding vibrational eigenproperties.<sup>1</sup> Techniques based on propagation, on sophisticated eigenvalue techniques, and even on basis set expansion have resulted in accurate eigenvalue determination for relatively large vibrational systems.<sup>2–14</sup>

In the analogous electronic structure problem, use of mean field (Hartree–Fock) methods yields a very accurate and broadly applicable initial approximation. A series of well defined methods can be developed to improve energies and wave functions based either on use of the variational principle (configuration interaction and multiconfiguration techniques) or on the use of perturbation theory (Møller–Plesset methods). Static mean field methods for the vibrational problem have been applied fairly extensively, including a recent application to a small protein system.<sup>15</sup> Analogous dynamic mean field models of even broader applicability can be used to provide information both on nuclear structure and on dynamical behavior including excitations and time evolution.<sup>16</sup>

Improvement of SCF techniques for vibrations using configuration interaction models appeared more than a decade ago.<sup>17,18</sup> To our knowledge, however, perturbation methods for extending the accuracy of mean field calculations in the vibrational context have not yet appeared. In this paper we examine the behavior of Møller–Plesset perturbation theory for vibrational problems. Under the normal cave-

ats concerning perturbation series we find that the method is of high accuracy, exhibits rapid and effective convergence, and is easily applied. It thus appears to be a competitive and useful method for obtaining high accuracy vibrational data from known potentials.

The formulation for vibrational problems is given in Sec. II; calculations on a number of small molecule systems appear in Sec. III, and some comments are made in Sec. IV.

## II. THEORY

Møller–Plesset perturbation theory (MPPT) is the most obvious way to correct, using perturbation methods, the self-consistent field (SCF) approach. Although numerous reviews of vibrational SCF calculations exist,<sup>19–22</sup> we give here a brief overview. Along with a discussion of SCF we state the equations for MPPT, which is just Rayleigh–Schrodinger perturbation theory with the choice of the perturbation Hamiltonian being the full Hamiltonian minus the SCF Hamiltonian.

### A. Molecular vibration theory: Equations and coordinates

The full Hamiltonian using the Born–Oppenheimer approximation for vibrational dynamics can be written as

$$\left[ \frac{1}{2} g^{1/4} \sum_{i,j} p_i g^{-1/2} g^{ij} p_j g^{1/4} + V(\mathbf{r}) \right] \Psi = E \Psi, \quad (1)$$

where  $p_i$  and  $p_j$  are momentum operators,  $g$  is the kinetic energy coupling tensor, and  $g^{ij}$  denotes the elements of the inverse of  $g$ .<sup>23</sup> The vector,  $\mathbf{r}$ , is the set of internal coordinates.

This equation can be very complex in these coordinates because the kinetic energy coupling tensor is usually quite

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cumbersome. It is much more convenient to carry out the analysis in a set of coordinates where the kinetic energy operator is uncoupled. Accordingly we use normal coordinates, a set of vibrational coordinates that diagonalizes the kinetic energy operator as well as the quadratic terms in the potential energy operator. The procedure for finding these coordinates is conceptually quite simple. As a first step we assume that the function  $V(\mathbf{r})$  is analytic, and write it as a Taylor series in the internal coordinates. The second order derivatives of the Taylor expanded surfaces are collected in the second order tensor  $F^{ic}$ . The  $B$  operator transforms the internal coordinates to cartesian coordinates,  $\mathbf{x}$ , by the mapping,  $\mathbf{r} = B\mathbf{x}$ .<sup>23–25</sup>

We then define a set of *mass weighted* coordinates by the transformation  $\mathbf{q} = M^{1/2}\mathbf{x}$ , where  $M^{1/2}$  is a  $3N_a$  ( $N_a$  being the number of atoms in the molecule of interest, the number of vibrational modes is  $3N_a - 6$  which is also the number of normal coordinates which we denote as  $N$ ) diagonal matrix and the elements are the square root of the atom masses, i.e.,  $\text{diag}[m_1^{1/2}, m_1^{1/2}, m_1^{1/2}, \dots, m_N^{1/2}, m_N^{1/2}, m_N^{1/2}]$ . By matrix multiplication  $F^{ic}$  is transformed to Cartesian coordinates and then to mass weighted coordinates, resulting in a tensor of mass weighted second order force constants

$$F^{mw} = M^{-1/2} B^T F^{ic} B M^{-1/2}. \quad (2)$$

We denote mass weighted coordinates as  $\mathbf{q}$ . This matrix is diagonalized to yield the normal mode frequencies and displacement vectors. These are, respectively, related to the eigenvalues and eigenvectors of  $F^{mw}$ . If the eigenvalues of  $F^{mw}$  are  $\lambda$  then the harmonic frequencies,  $\omega$ , are related by

$$\omega = \sqrt{\frac{\lambda}{4\pi^2}}. \quad (3)$$

The eigenvectors of  $F^{mw}$  are collected into a tensor,  $L$ ; the normal coordinates are found by the transformation  $\mathbf{q} = L\mathbf{Q}$ . We can then calculate other coordinate transformations; for instance, normal coordinates and internal coordinates are related by

$$\mathbf{Q} = T\mathbf{r}, \quad (4)$$

where  $T = (BM^{-1/2}L)^{-1}$ .

The kinetic energy operator in the Schrodinger equation in these coordinates is separable. The masses in the kinetic energy operator are now absorbed into the coordinates. The full Schrodinger equation in this set of coordinates can now be written as

$$-\frac{\hbar^2}{2} \sum_k \left[ \frac{\partial^2 \Psi}{\partial Q_k^2} \right] + V(\mathbf{Q})\Psi = E\Psi. \quad (5)$$

The Hamiltonian is the sum of the kinetic energy operators plus the full potential energy operator which includes mode coupling terms.

There are two ways to define the potential in this set of coordinates. One way is to curve fit the original potential to these coordinates. A point in internal coordinate space is transformed to normal coordinate space and the correspond-

ing energy value is the data point. Assuming again that the potential function has polynomial form, these data are fit using standard regression techniques.<sup>26,27</sup>

A second is to use the chain rule to get the potential parameters in the normal coordinates. For example, the third order potential energy derivatives in normal coordinates are given by

$$\begin{aligned} \frac{\partial^3 V(\mathbf{Q})}{\partial Q_a \partial Q_b \partial Q_c} &= \sum_l^N \sum_m^N \sum_n^N \frac{\partial^3 V(\mathbf{r})}{\partial r_l \partial r_m \partial r_n} \\ &\times \sum_s^{3N_a} B_{ls} M_{ss}^{1/2} L_{sa} \sum_t^{3N_a} B_{mt} M_{tt}^{1/2} L_{tb} \\ &\times \sum_v^{3N_a} B_{nv} M_{vv}^{1/2} L_{vc}, \end{aligned} \quad (6)$$

where  $V(\mathbf{r})$  is the potential in arbitrary form,  $B_{ij}$  denotes the transformation from Cartesian coordinate  $j$  to internal coordinate  $i$ ,  $M_{ii}^{1/2}$  is an element in the diagonal matrix of the mass square roots, and  $L_{ij}$  is the transformation from normal coordinate  $j$  to mass weighted coordinate  $i$ .  $V(\mathbf{Q})$  is to be thought of as a Taylor series of these types of terms. Derivatives where all the indices on the normal coordinates are equal are called diagonal terms. On the other hand, derivatives where the indices on the normal coordinates are not all equal are called off-diagonal. It is the off-diagonal terms that couple the modes. Therefore, we think of  $V(\mathbf{Q})$  as being the sum of diagonal and off-diagonal terms.

## B. The SCF scheme

The SCF approximation assumes that the solution to the Schrodinger equation for the entire  $N$ -dimensional system can be written as a product of single mode wave functions. That is,

$$\Psi^{\text{SCF}}(\mathbf{Q}) = \prod_{k=1}^N \phi^k(Q_k). \quad (7)$$

Then this is substituted into the full equation, yielding  $N$  single mode equations. The coupling terms in the potential in these equations are approximated by a mean taken over all other modes.

That is, we define the potential as the sum of diagonal and off-diagonal parts where the diagonal terms for mode  $k$  are terms like  $V_{k\alpha} Q_k^\alpha$  and off-diagonal terms are like  $V_{k\beta j\nu} Q_k^\beta Q_j^\nu$ . In mode  $k$  we approximate  $Q_j^\nu$  by its quantum average,  $\langle Q_j^\nu \rangle = \langle \phi^j | Q_j^\nu | \phi^j \rangle$ .<sup>28</sup> The single mode equations can be written as

$$h_{\text{SCF}}(Q_k) \phi^k = -\frac{\hbar^2}{2} \frac{\partial^2 \phi^k}{\partial Q_k^2} + V_k^{\text{SCF}}(Q_k) \phi^k = \epsilon_k \phi^k, \quad (8)$$

where the single mode effective potential  $V_k^{\text{SCF}}$  is given by the integrated Taylor series

$$V_k^{\text{SCF}}(Q_k) = \left\langle \prod_{j \neq k}^N \phi^j | V(Q_k; Q_j) | \prod_{j \neq k}^N \phi^j \right\rangle, \quad (9)$$

where  $V(Q_k; Q_j)$  denotes terms that depend either on  $k$  alone, *diagonal terms*, or on both  $k$  and  $j$ , *off-diagonal terms*.  $V_k^{\text{SCF}}(Q_k)$  is a function of  $Q_k$  only; the other  $Q_j$ 's are now represented by *constants*, their quantum averages. This approximation transforms the problem of solving the eigenvalue equation on a  $N$ -dimensional hyperplane to solving  $N$  one dimensional problems.

The total energy of the multimode system is found by summing the eigenvalues for each of the single mode equations and subtracting the terms added more than once in this summation. For instance a term like  $V_{112}Q_1^2Q_2$  would appear in the single mode equation for both modes 1 and 2. When the single mode energies are summed the energy from this term is counted twice. Therefore, we subtract it once. The final SCF total energy is calculated using the formula

$$E = \sum_{k=1}^N \epsilon_k - (l-1) \left\langle \prod_{k=1}^N \phi^k | V_{\text{off-diagonal}}(\mathbf{Q}) | \prod_{k=1}^N \phi^k \right\rangle, \quad (10)$$

where  $l$  is the number of single mode equations in which a particular off-diagonal term appears.

The equations are solved numerically and self-consistently. There are many advanced methods for solving the SCF equations.<sup>29–31</sup> Since our interest here is the

Möller–Plesset perturbation theory, we kept our SCF solution simple and just used finite differences.

### C. Perturbation theory

We employ the Möller–Plesset theory in a fashion analogous to how it is used in electronic structure problems.<sup>32</sup> The perturbation Hamiltonian is defined as the full Hamiltonian minus the sum of the single mode SCF Hamiltonians, i.e.,  $V' = H - \sum_k h_{\text{SCF},k}$ . This perturbation Hamiltonian is inserted into the normal Rayleigh–Schrodinger expressions for the first, second, third, and fourth order perturbation energy corrections which are<sup>33,34</sup>

$$E_i^{(1)} = \langle i | V' | i \rangle, \quad (11)$$

$$E_i^{(2)} = \sum_{n \neq i} \frac{|\langle i | V' | n \rangle|^2}{(E_i^{(0)} - E_n^{(0)})}, \quad (12)$$

$$E_i^{(3)} = \sum_{n \neq i} \left[ \sum_{m \neq n \neq i} \frac{\langle i | V' | n \rangle \langle n | V' | m \rangle \langle m | V' | i \rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} \right] - E_i^{(1)} \sum_{n \neq i} \frac{|\langle i | V' | n \rangle|^2}{(E_i^{(0)} - E_n^{(0)})^2}, \quad (13)$$

and

$$E_i^{(4)} = \sum_{n \neq i} \left[ \sum_{m \neq n \neq i} \left[ \sum_{l \neq m \neq n \neq i} \frac{\langle i | V' | n \rangle \langle n | V' | m \rangle \langle i | V' | l \rangle \langle m | V' | l \rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_l^{(0)})} + \frac{E_i^{(1)}(\langle i | V' | n \rangle)^2 \langle i | V' | l \rangle}{(E_i^{(0)} - E_n^{(0)})^2 (E_i^{(0)} - E_l^{(0)})} \right] + \frac{E_i^{(1)} \langle n | V' | m \rangle \langle i | V' | n \rangle \langle i | V' | m \rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})^2} + \frac{(\langle i | V' | n \rangle)^2 (\langle i | V' | m \rangle)^2}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})^2} \right] + \frac{(E_i^{(1)})^2 (\langle i | V' | n \rangle)^2}{(E_i^{(0)} - E_n^{(0)})^3}, \quad (14)$$

respectively. The kets  $|i\rangle$ ,  $|n\rangle$ ,  $|m\rangle$ , and  $|l\rangle$  denote the entire product wave function of the reference level and the excited states, respectively.  $E_i^{(0)}$ ,  $E_n^{(0)}$ ,  $E_m^{(0)}$ , and  $E_l^{(0)}$  are the sums of the single mode energies in the reference and excited virtual states, respectively.

In this formulation all the diagonal terms cancel and only the off-diagonal potential terms remain. Hence, the perturbation Hamiltonian operator is a sum where the terms are of the form

$$V' = \sum_{kl'm''} V_{kkl}(Q_k^2 Q_l - \langle Q_k^2 \rangle Q_l - Q_k^2 \langle Q_l \rangle) + V_{kkkl}(Q_k^3 Q_l - \langle Q_k^3 \rangle Q_l - Q_k^3 \langle Q_l \rangle) + V_{klm}(Q_k Q_l Q_m - Q_k \langle Q_l \rangle Q_m - \langle Q_m \rangle Q_k Q_l - \langle Q_k \rangle Q_l Q_m - \langle Q_k \rangle \langle Q_l \rangle Q_m) + \dots, \quad (15)$$

where the quantum averages are SCF averages. It should be noted that putting the perturbation Hamiltonian in the expression for the first order energy correction results in the same SCF energy correction calculated by  $(l-1) \langle \prod_{k=1}^N \phi^k | V_{\text{off-diagonal}}(\mathbf{Q}) | \prod_{k=1}^N \phi^k \rangle$ . Likewise, the zeroth order energy in this perturbation scheme is just the sum of the single mode energies.

When  $V'$  is put into these expressions we find that important simplifications occur which we state in the following proposition:

**Proposition 1:** Given a  $\mathcal{K}$ -body term,  $V_{\mathcal{K}}$ , involving a set of modes  $\mathcal{N}$ , if any mode that is not in  $\mathcal{N}$  is excited, then the integral  $\langle i | V_{\mathcal{K}} | n \rangle$ , where  $i$  and  $n$  denote the entire product wave function for the reference and excited state, respectively, is zero. On the other hand, if modes that are in  $\mathcal{N}$  are excited and the modes are partitioned into two sets,  $S$  and  $T$ , where the  $M$  excited modes ( $0 \leq M \leq \mathcal{K}$ ) are put into  $S$  and the remaining  $\mathcal{K}-M$  unexcited modes into  $T$ , then the integral of this  $\mathcal{K}$ -body term takes the form

$$\left( \prod_S \bar{Q}_s^{\sigma_s} \right) \left( \prod_T \langle Q_t^{\tau_t} \rangle \right) (1 + M - \mathcal{K}) \quad (16)$$

where  $\sigma_s$  and  $\tau_t$  are exponents in  $V_{\mathcal{K}}$  on coordinate  $s$  and  $t$ , respectively.  $\bar{Q}_s^{\sigma_s}$  is a quantum transition moment and  $\langle Q_t^{\tau_t} \rangle$  is an SCF expectation value. The products are taken over whatever modes are in sets  $S$  and  $T$ .

This is just a generalization of Brillouin's theorem for multibody terms and only applies to transitions from the

ground state. There are corollaries that can be written for *hot* transitions or integrals that are calculated at the MP3 and MP4 levels. Using this analytic result leads to simplifications in the computing perturbation energies and wave functions.

### III. COMPUTATIONS AND RESULTS

The Schrodinger equations in this study are solved using finite differences. Using the fourth order operator results in

$$-\frac{\hbar^2}{2} \left[ \frac{-\phi_{i+2}^k + 16\phi_{i+1}^k - 30\phi_i^k + 16\phi_{i-1}^k - \phi_{i-2}^k}{12\delta^2} \right] + V_k^{\text{SCF}}(Q_k)_i \phi_i^k = \epsilon_k \phi_i^k. \quad (17)$$

This treatment turns the integro-differential eigenvalue equation into a matrix eigenvalue problem,  $A\phi^k = \epsilon_k \phi^k$ . In all our SCF computations the end point of the interval for the normal coordinate was estimated by the expression,  $S\lambda_k^{-0.25}$ , where  $S$  is some prefactor, usually 6.00, and  $\lambda_k$  is related to the second order force constant for mode  $k$ . This expression is found by solving for the zeroes of the ground state harmonic oscillator wave function. Since the error is determined by  $\delta Q$  we kept it constant for each mode but varied the number of points.

The proposition above guides the implementation of MP. Each combination of modes has to be parsed for each combination of excitations. Specifically, we first select two modes,  $k$  and  $l = k + 1$ ; the two mode perturbation integral is calculated for these two modes for each combination of excitation that we select. From our proposition there is only one such computation for the two mode terms. We then select a mode,  $m \neq k \neq l$ , and calculate the perturbation integrals for the three body terms. Our proposition tells us that we must calculate the case where one mode is excited and when all three modes are excited. Four mode and higher term perturbation integrals are calculated analogously. Care must be taken in this calculation to allow only one permutation of mode combinations.

As a final technical detail we mention that the second, third, and higher correction terms in the perturbation series are themselves infinite series in excitations. We found that for each mode it is only necessary to include states bracketing the reference state by three quantum levels both above and below to achieve convergence. This can be understood by analyzing the integrals using raising and lowering operators and assuming harmonic wave functions.

We used various potentials in this study. Early testing was done with the two mode Henon–Heiles potential.<sup>35</sup> We also used a model three mode potential also studied by Christoffel.<sup>36</sup> Since the kinetic energy operators in these Hamiltonians are already diagonal, no initial matrix diagonalization to make a coordinate transformation from internal to mass weighted normal coordinates is needed. We used the method on a water potential given by Kaupi and Halonen.<sup>37</sup> We also performed our calculations using the potential for formaldehyde provided by Bowman via POLYMODE and its new update.<sup>38,39</sup> In each case we compare our results to es-

TABLE I. Henon–Heiles potential.  $H = -1/2(\partial^2/\partial Q_1^2 + \partial^2/\partial Q_2^2) + 1/2\omega_1^2 Q_1^2 + 1/2\omega_2^2 Q_2^2 + \lambda(Q_1 Q_2^2 + \eta Q_1^3)$ ;  $\omega_1^2 = 0.293\,75$ ,  $\omega_2^2 = 2.125\,81$ ,  $\lambda = -0.1116$ ,  $\eta = 0.084\,14$ . Shown are the total energies at each level of approximation as well as the correction contribution at each level.  $E_i$  is the total energy. The error is calculated with the respect to the virtual CI total energy.

	(00)	(10)	(20)	(01)
Et Harmonic	1.000 00	1.541 99	2.083 98	2.458 02
Et SCF	0.992 47	1.518 98	2.036 32	2.421 68
VSCF (MP1)	0.008 82	0.016 66	0.025 30	0.061 63
MP2	-0.000 83	-0.003 00	-0.005 38	-0.002 72
MP3	0.000 00	0.000 00	0.000 03	-0.000 03
MP4	0.000 00	-0.000 02	-0.000 08	-0.000 01
Et MP2	0.991 64	1.515 98	2.030 94	2.418 97
Et MP3	0.991 64	1.515 99	2.030 96	2.418 93
Et MP4	0.991 64	1.515 97	2.030 88	2.418 94
Et VCI	0.991 63	1.515 95	2.030 85	2.418 91
% Error SCF	-0.085	-0.200	-0.269	-0.115
% Error MP2	-0.001	-0.002	-0.004	-0.002
% Error MP3	-0.001	-0.002	-0.005	-0.001
% Error MP4	-0.001	-0.001	-0.002	-0.001

entially exact quantum eigenstates calculated by virtual CI. We present our results in the succeeding subsections.

#### A. Model potentials

The Henon–Heiles potential is a simple potential on which to test quantum vibration calculations. Its eigensystem is well characterized both analytically and numerically. The model can describe a three mode system like a triatomic molecule, freezing the bend coordinate. In this case and truncating the potential to third order, one gets something akin to the Henon–Heiles Hamiltonian. Table I shows the results for this two mode system. We have reproduced SCF eigenvalues as calculated by Bowman.<sup>35</sup> For the states presented the average error of the SCF energy with respect to the quantum exact energy is less than 1%. Our MP calculations produce the quantum exact energy to five figures even at the MP2 level. It can also be seen for the (0,0) state that the perturbation series is convergent since the MP2 correction is one order of magnitude less than the MP1 correction; likewise the MP3 and MP4 corrections are a couple of orders of magnitude less than the MP2 correction.

We get similar results with the model 3 mode potential as can be seen in Table II. Systematically, for all excited states, the MP4 correction exceeds the MP3, which might suggest convergence difficulties in the MP series. Nonetheless, looking at the other states, we do see that the series is converging at third order and that the error is reduced by the MP corrections.

#### B. H<sub>2</sub>O

To test this perturbative method in a real molecular system we used the potential surface recently presented by Kaupi and Halonen.<sup>37</sup> A representative sample of our results is presented in Table III. Our errors are calculated here with respect to virtual CI eigenstates that we calculated from this potential. This is discussed in the next section.

TABLE II. Model 3 mode system studied in Ref. 36.  $H = -1/2(\partial^2/\partial Q_1^2 + \partial^2/\partial Q_2^2 + \partial^2/\partial Q_3^2) + 1/2\omega_1^2 Q_1^2 + 1/2\omega_2^2 Q_2^2 + 1/2\omega_3^2 Q_3^2 + 2\lambda \eta Q_1^3 + 2\mu \zeta Q_2^3 + \lambda Q_1 Q_2^2 + \mu Q_2 Q_3^2$ . Parameters are the same as used by Christoffel,  $\omega_1^2=0.49$ ,  $\omega_2^2=1.69$ ,  $\omega_3^2=1.00$ ,  $\lambda=\mu=-0.10$ , and  $\eta=\zeta=0.10$ . Errors are computed with respect to our VCI calculations which essentially reproduces the numbers reported by Christoffel.

	(000)	(001)	(010)	(100)	(101)	(200)
Et Harmonic	1.5000	2.5000	2.8000	2.2000	3.2000	2.9000
Et SCF	1.4951	2.4883	2.7780	2.1884	3.1815	2.8784
VSCF (MP1)	0.0067	0.0199	0.0368	0.0103	0.0237	0.0140
MP2	-0.0013	-0.0025	-0.0061	-0.0032	-0.0047	-0.0052
MP3	0.0000	0.0000	-0.0002	0.0000	0.0000	0.0000
MP4	0.0000	0.0000	-0.0005	0.0000	0.0001	-0.0001
Et MP2	1.4938	2.4857	2.7720	2.1852	3.1768	2.8732
Et MP3	1.4938	2.4857	2.7718	2.1852	3.1768	2.8732
Et MP4	1.4938	2.4857	2.7713	2.1852	3.1768	2.8732
Et VCI	1.4938	2.4857	2.7718	2.1852	3.1783	2.8732
% Error SCF	-0.0852	-0.1023	-0.2247	-0.1459	-0.1013	-0.1815
% Error MP2	-0.0004	-0.0001	-0.0063	-0.0007	0.0462	-0.0017
% Error MP3	-0.0003	0.0004	0.0000	-0.0005	0.0473	-0.0017
% Error MP4	0.0000	0.0003	0.0179	0.0003	0.0454	0.0008

For the states on the left of the table the Möller–Plesset series converges rapidly and the error is reduced. For the states on the right, (2,2,2) and (3,2,2), which are high energy states, the series does not converge properly. This is to be expected and the explanation is that as we get to levels where the density of states is high, the apparent divergences occur because of singularities caused by near zero values in the denominator of the expansion terms. For example, when (2,2,2) is the reference state, state  $i$ , the MP0 energy for virtual state (0,2,4) is very near to the MP0 energy of (2,2,2). Likewise, the MP0 energy for reference state (3,2,2) is nearly

degenerate with the MP0 energy for virtual state with (5,2,0) which contributes to the divergence of the MP series in this case.

### C. H<sub>2</sub>CO

Recently, there has been a series of reports on the vibrations of formaldehyde.<sup>40–43</sup> Accordingly we applied our method to this molecule to demonstrate that it can be used in system of this size with some success. The results from our calculations are shown in Table IV. We compare our MP

TABLE III. Results for H<sub>2</sub>O using surface in Kaupi and Halonen (Ref. 37). The total energy for the harmonic, SCF, MP2, and MP3 approximations is given. All energies are given in wave numbers (cm<sup>-1</sup>). Errors are computed with respect to our VCI energies. Comparing our calculations directly to those reported by Kaupi and Halonen introduces a slight technical problem. They included vibration-rotation coupling in their analysis. Our calculations explicitly exclude those effects. Therefore we should expect residual errors to persist in our energies with respect to theirs. However our MP energies reduce the error with respect to their numbers (data not shown).

	(000)	(010)	(020)	(030)	(001)	(222)	(322)
Et Harmonic	4705.89	6350.41	7994.92	9639.43	8640.50	23 529.47	27 362.14
Et SCF	4679.84	6294.99	7878.53	9426.42	8507.42	23 114.00	26 933.05
Vscf (MP1)	-62.76	-72.79	-85.27	-100.73	-444.33	-804.37	-577.11
MP2	-14.49	-16.90	-21.61	-28.22	-37.14	-1607.04	236.99
MP3	0.73	0.95	0.95	0.93	0.61	-15 195.54	-6468.06
MP4	-0.15	-0.34	-2.26	7.51	1.50	3 070 455.51	-1 178 025.43
Et MP2	4665.35	6278.08	7856.91	9398.20	8470.28	21 506.96	27 170.03
Et MP3	4666.08	6279.04	7857.87	9399.13	8470.89	6311.42	20 701.98
Et MP4	4665.93	6278.70	7855.61	9406.64	8472.39	3 076 766.94	-1 157 323.46
Et VCI	4665.62	6278.39	7857.06	9398.34	8470.93		
% Error SCF	-0.3	-0.3	-0.3	-0.3	-0.4		
% Error MP2	0.0	0.0	0.0	0.0	0.0		
% Error MP3	0.0	0.0	0.0	0.0	0.0		
% Error MP4	0.0	0.0	0.0	-0.1	0.0		

TABLE IV. Results for H<sub>2</sub>CO from the potential used by Romanowski, *et al.* (Ref. 38). The SCF-VCI energies shown are the results of our calculations and essentially reproduce those reported in Ref. 38. The errors are calculated with respect to these energies. All energies are given in wave numbers (cm<sup>-1</sup>).

	(000000)	(000100)	(000001)	(001000)	(010000)	(100000)	(100001)	(000010)	(110001)
Et Harmonic	5864.5	7052.8	7134.0	7408.5	7642.3	8802.0	10071.4	8876.6	11849.2
Et SCF	5796.3	6947.6	7044.8	7302.9	7546.6	8610.4	9824.9	8640.2	11568.1
VSCF (MP1)	95.2	146.0	129.1	135.1	111.2	161.2	232.3	492.3	258.5
MP2	-18.4	-15.3	-25.9	-19.8	-10.0	-25.2	-48.1	-3101.4	-52.0
MP3	-7.8	-25.7	-9.3	-37.4	-13.3	8.2	-104.1	-27316.6	125.5
MP4	0.7	4.0	1.3	22.8	6.0	-1.0	-7987.8	65988.0	1564.9
Et MP2	5777.8	6932.2	7018.9	7283.1	7536.6	8585.2	9776.8	5538.8	11516.1
Et MP3	5770.0	6906.6	7009.6	7245.7	7523.3	8593.4	9672.7	-21777.7	11641.6
Et MP4	5770.7	6910.5	7010.9	7268.4	7529.3	8592.4	1684.9	44210.2	13206.5
Et VCI	5777.3	6937.8	7022.9	7277.5	7524.5	8558.8	9783.7	8635.0	
% Error SCF	-0.3	-0.1	-0.3	-0.3	-0.3	-0.6	-0.4	-0.1	
% Error MP2	0.0	0.1	0.1	-0.1	-0.2	-0.3	0.1	35.9	
% Error MP3	0.1	0.5	0.2	0.4	0.0	-0.4	1.1	352.2	
% Error MP4	0.1	0.4	0.2	0.1	-0.1	-0.4	82.8	-412.0	

results to our SCF-VCI calculations that essentially reproduced those performed by Romanowski.<sup>38</sup> In all but the (0,1,0,0,0) state the MP2 energy is in less error than the MP3 energy. Moreover, the MP series for the four states in the middle of the table, while still being quite accurate, apparently do not converge at the third order. This is another example of the nonvariational character of perturbation series. Nonetheless in all the states shown MP treatment does reduce the error in the SCF energies.

#### IV. DISCUSSION

Along with the perturbative method to include correlation we can do virtual CI calculations. The virtual state CI eigenspectrum is the spectrum of the matrix  $A$  where the elements are defined as  $A_{ij} = \delta_{ij}E_i^{(0)} + V_{ij}$ , where  $E_i^{(0)}$  is the MP0 energy as defined above and  $V_{ij}$  is the integral  $\langle i|V'|j\rangle$ . In the ground state we can compare directly the MP energy and the spectrum of  $A$ . For higher level states it may become necessary to calculate the CI coefficients for state identification. We took equivalence of the MP3 and VCI energies in the ground state as confirmation that our SCF/MP method gives sufficient approximation to the exact quantum energy. In our initial calculations we found that timings for MP calculations were generally longer than those for VCI, even in large molecules where the necessary number of configurations is higher. However, there are many improvements in our implementation underway, and already the timings for MP are competitive with VCI. We are confident that this method can be made surely faster than VCI.

Divergence of the MP series is caused by near degeneracies in the MP0 energies of states in the perturbation expansion. This can be easily seen in the mathematical character of the denominators of the perturbation terms. Hence, divergence is expected to occur at energy states around resonances or where the density of states is high. Specifically, the state density to be visualized by the reader is the potentials for each mode plotted on the same graph with their respective single mode energy levels superimposed. The MP0 energies are summations of these energy levels in various com-

binations. As the number of modes, i.e., the size and complexity of the molecule, increases it should be apparent that there is a greater chance that a particular combination of these energy levels will be equal or nearly equal to another combination. Furthermore, because for the MP2 expansion term the denominator is  $\Delta E = E_i^{(0)} - E_n^{(0)}$  and for the MP3 and MP4 terms the denominators contain terms like  $(\Delta E)^2$  and  $(\Delta E)^3$ , respectively, it is evident that at higher levels of perturbation expansion we can expect divergence to occur at a lower density of states.

One interesting feature gained from these calculations and those on van der Waals clusters is that when the anharmonicities are weak, i.e., the coupling force constants are very small the MP series behaves better.<sup>44</sup> In this case it appears that if the denominator is small, counteraction is provided by the smallness of the numerator. It is therefore difficult to give any guidance as to how nearly degenerate two states have to be before a problem arises. It depends on the physical system under study and, importantly, how the calculation is coded and how the computer deals with overflow.

There are several ways to correct to this degeneracy problem. First, it is important to understand that of the many combinations of states included in the summations for each perturbation term, it only takes one to the cause the entire series to diverge. Indeed, in our calculations on water only two combinations caused a problem; and for formaldehyde, with many more possible combinations, only five near degeneracies were found. This is of course dependent on our tolerance criterion. We could simply include a flag in our code to exclude any divergence producing states from the summation. If that is unacceptable an appeal can be made to degenerate perturbation theory or any general CI extension of perturbation theory. Recently, a method was reported for removing degeneracies from perturbation expansions.<sup>45,46</sup> We have not yet implemented this method in our study but it is the logical next step.

In addition to energies we are confident that we can calculate MP corrections to properties such as mean and mean-

square displacements. We hope to soon report property corrections to the SCF calculations on BPTI.<sup>15</sup>

## V. CONCLUSION

We have introduced a new method to include correlation energy in vibrational SCF calculations. We use Möller–Plesset theory (to MP4) in an exactly analogous way to its use in electronic structure calculations. For low-lying states and for states away from resonances the method converges rapidly and reduces errors in the energy. Finding such states that are away from resonance conditions becomes more difficult in more complex molecules with more vibrational modes. For high energy states the perturbation series diverges and the method fails. Generally, the MP2 level gives very accurate energies and additional correction made in the higher level series is not substantial. Because of this fact and because of the degeneracy problem of higher energy states, we believe that including MP3 and MP4 level terms is not yet profitable.

In the future we will implement methods to remove degeneracies and to calculate perturbation wave functions and molecular properties.

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