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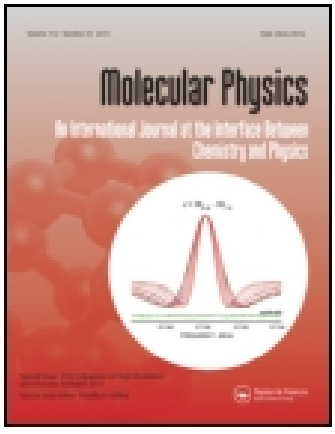

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A hybrid variational-perturbational nuclear motion algorithm

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INVITED ARTICLE

A hybrid variational–perturbational nuclear motion algorithm

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A hybrid variational–perturbational nuclear motion algorithm based on the perturbative treatment of the Coriolis coupling terms of the Eckart–Watson kinetic energy operator following a variational treatment of the rest of the operator is described. The algorithm has been implemented in the quantum chemical code DEWE. Performance of the hybrid treatment is assessed by comparing selected numerically exact variational vibration-only and rovibrational energy levels of the C_2H_4, C_2D_4, and CH_4 molecules with their perturbatively corrected counterparts. For many of the rotational–vibrational states examined, numerical tests reveal excellent agreement between the variational and even the first-order perturbative energy levels, whilst the perturbative approach is able to reduce the computational cost of the matrix-vector product evaluations, needed by the iterative Lanczos eigensolver, by almost an order of magnitude.

Keywords: Eckart–Watson Hamiltonian; variational–perturbational approach; nuclear motion theory; C_2H_4; C_2D_4; CH_4

1. Introduction

Accurate prediction of large numbers of rotational–vibrational energy levels of medium-sized molecules is one of the challenging tasks of nuclear motion theory, with immediate applications in high-resolution molecular spectroscopy. The accuracy required from the computations often necessitates that determination of the energy levels, and the associated wavefunctions, is based on the variational principle. Due to considerable methodological advances, and the availability of considerable computational resources, fully variational approaches [1,2] have gained considerable popularity, despite the associated relatively high cost. Fully perturbational approaches based on second-order vibrational–perturbation theory (VPT2) [3–5], after more than two decades of their first thorough testing [6,7], have become almost routine, especially after making them available in standard electronic structure packages. There have also been attempts to go to higher orders of vibrational–perturbation theory [3,8,9], as well as to extend VPT2 by taking into consideration all cubic and quartic resonances in a perturbation–resonance approach [10]. Unlike VPT2, these perturbation-based approaches gained only limited popularity. Thus, there is still a lot of room for suggesting and investigating algorithms more elaborate and accurate than VPT2, but considerably less costly than a fully variational treatment. One such possibility is investigated here, whereby certain (simpler) terms of a rotational–vibrational Hamiltonian are treated variationally, but the more complex (and costly) ones only perturbationally.

A possible and widely employed [1] choice for representing the rotational–vibrational kinetic energy in internal coordinates is the general and exact Eckart–Watson kinetic energy operator [11–13], which is based on rectilinear vibrational (normal) coordinates and the Eckart embedding. It works well for semi-rigid molecules and at lower excitations. Many research groups have developed methods and codes for the solution of the time-independent Schrödinger equation based on the full Eckart–Watson Hamiltonian (EWH) [14–30]. An early but powerful implementation of a *simplified* EWH for larger systems was published in Refs [17] and [18].

The in-house quantum chemical code DEWE [24,25,28] provides an efficient implementation of the full EWH for rotational–vibrational computations employing a discrete variable representation (DVR) [31,32] and an iterative Lanczos eigensolver algorithm [33]. An expensive part of the variational computations based on the EWH concerns the evaluation and utilisation of matrix elements involving the Coriolis coupling operator (Equation (1), *vide infra*). In the first paper reporting the DEWE protocol [24], it was investigated how neglecting certain terms of the vibrational EWH affects the computed vibrational energy levels. The results obtained made clear that full inclusion of the Watson term (Equation (1), *vide infra*) in the variational procedure is inexpensive and its neglect can result in corrections up to a few cm^{-1}. Furthermore, it was shown that completely neglecting the vibrational Coriolis coupling term (Equation (1), *vide infra*) has an effect of the order of a few ten or

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even a hundred cm^{-1}; thus, this term of the EWH cannot be fully neglected. The next, less dramatic step is to consider the Coriolis coupling terms perturbationally. This strategy is followed during this study. It is important to note that similar questions have been investigated by other research groups [17,18,34–39].

In summary, an expensive part of a variational nuclear motion computation based on the EWH and a DVR is connected to the matrix elements of the Coriolis coupling terms. Thus, the main focus of this work is the perturbative treatment of these two terms within a hybrid vibrational–perturbational approach. In order to assess the performance of our hybrid approach, we carried out pure vibrational as well as rotational–vibrational variational computations for the hexatomic ethylene (C_2H_4), fully deuterated ethylene (C_2D_4), and pentatomic methane (CH_4) molecules with either the exact or the chosen zeroth-order nuclear motion Hamiltonians and corrected the zeroth-order rotational–vibrational energy levels, employing the lowest orders of the well-known Rayleigh–Schrödinger perturbation theory (RSPT).

2. Theory

The DEWE program package [24,25,28] allows the solution of the time-independent nuclear motion Schrödinger equation. DEWE is based on the use of the exact and (almost) general Eckart–Watson kinetic energy operator [11–13], the DVR [31,32], and the iterative Lanczos eigensolver algorithm [33]. The rotational–vibrational EWH expressed in orthogonal, rectilinear vibrational coordinates is

$$\hat{H} = \frac{1}{2}\sum_{k=1}^{3N-6}\hat{P}_k^2 + \frac{1}{2}\sum_{\alpha\beta}(\hat{J}_\alpha - \hat{\pi}_\alpha)\mu_{\alpha\beta}(\hat{J}_\beta - \hat{\pi}_\beta) - \frac{\hbar^2}{8}\sum_{\alpha}\mu_{\alpha\alpha} + \hat{V} \quad (1)$$

for an N-atomic molecule with a non-linear reference configuration. In Equation (1), $\hat{P}_k = -i\hbar\frac{\partial}{\partial Q_k}$, where Q_k is the kth rectilinear vibrational coordinate, $\alpha, \beta = x, y, z$, $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are the body-fixed components of the total angular momentum operator, $\hat{\pi}_\alpha$ refers to components of the so-called [40] Coriolis coupling operator, $\mu_{\alpha\beta}$ stands for elements of the generalised inverse effective inertia tensor, the penultimate term of Equation (1) is the so-called Watson term, and $\hat{V}$ is the potential energy surface (PES). To move forward let us write the EWH as

$$\hat{H} = \hat{T}^v + \hat{T}^r + \hat{T}^{rv} + \hat{V}, \quad (2)$$

where the $\hat{T}^v$ vibrational, $\hat{T}^r$ rotational, and $\hat{T}^{rv}$ rovibrational Coriolis coupling kinetic energy operator terms are defined as

$$\hat{T}^v = \frac{1}{2}\sum_{k=1}^{3N-6}\hat{P}_k^2 + \frac{1}{2}\sum_{\alpha\beta}\hat{\pi}_\alpha\mu_{\alpha\beta}\hat{\pi}_\beta - \frac{\hbar^2}{8}\sum_{\alpha}\mu_{\alpha\alpha}, \quad (3)$$

$$\hat{T}^r = \frac{1}{2}\sum_{\alpha}\mu_{\alpha\alpha}\hat{J}_\alpha^2 + \frac{1}{2}\sum_{\alpha}\sum_{\beta>\alpha}\mu_{\alpha\beta}[\hat{J}_\alpha, \hat{J}_\beta]_+, \quad (4)$$

$$\hat{T}^{rv} = -\sum_{\alpha\beta}\mu_{\alpha\beta}\hat{\pi}_\beta\hat{J}_\alpha, \quad (5)$$

where $[\hat{J}_\alpha, \hat{J}_\beta]_+$ stands for the anticommutator of the $\hat{J}_\alpha$ and $\hat{J}_\beta$ operators. As a next step, the EWH is partitioned as the sum of the zeroth-order

$$\hat{H}^{(0)} = \frac{1}{2}\sum_{k=1}^{3N-6}\hat{P}_k^2 - \frac{\hbar^2}{8}\sum_{\alpha}\mu_{\alpha\alpha} + \hat{T}^r + \hat{V}, \quad (6)$$

and the perturbing

$$\hat{W} = \frac{1}{2}\sum_{\alpha\beta}\hat{\pi}_\alpha\mu_{\alpha\beta}\hat{\pi}_\beta + \hat{T}^{rv} \quad (7)$$

operators. The rationale behind this partitioning is as follows: (1) The zeroth-order part contains all the single sums as well as a double-sum term involving an anticommutator, as evaluation and subsequent use of the matrix elements corresponding to the latter term is still relatively inexpensive. (2) The magnitude of the effect of the two Coriolis coupling terms (Equation (7)) on the rovibrational energies is relatively small when compared to terms put into the zeroth-order kinetic energy operator. (3) It is also important to note that as the $\mu_{\alpha\beta}$ operators are equal to the components of the generalised inverse inertia tensor, the effect of $\hat{W}$ becomes smaller if the size of the molecule and/or the masses of the nuclei increase.

The first step in the proposed hybrid variational–perturbational approach is the variational solution of the zeroth-order

$$\hat{H}^{(0)}\Psi_i^{(0)} = E_i^{(0)}\Psi_i^{(0)} \quad (8)$$

time-independent rotational–vibrational Schrödinger equation according to the usual DEWE algorithm [24,25,28]. Over the course of the Lanczos iteration, a large number of $\mathbf{H}^{(0)} \cdot \mathbf{x}$ matrix–vector products have to be evaluated, where $\mathbf{x}$ represents vectors appearing in the Lanczos algorithm. As the zeroth-order Hamiltonian lacks the most expensive Coriolis coupling terms (Equation (7)), the cost associated with the evaluation of the $\mathbf{H}^{(0)} \cdot \mathbf{x}$ matrix–vector products is reduced substantially, approaching an order of magnitude, for the test cases examined and when compared to the evaluation of the $\mathbf{H} \cdot \mathbf{x}$ products employing the EWH matrix.

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The next step employs the $\Psi_i^{(0)}$ zeroth-order nuclear-motion wavefunctions to compute the

$$W_{ij}^0 = \langle \Psi_i^{(0)} | \hat{W} | \Psi_j^{(0)} \rangle \quad (9)$$

matrix elements and correct the $E_i^{(0)}$ and $\Psi_i^{(0)}$ zeroth-order energy levels and wavefunctions according to RSPT. As the computation of $\mathbf{W}^0$ requires the evaluation of only a few $\mathbf{W} \cdot \mathbf{x}$ matrix–vector products, the cost of computing the W_{ij}^0 matrix elements is negligible compared to that of the solution of the unperturbed time-independent rotational–vibrational Schrödinger equation. The current implementation allows the determination of first- and second-order perturbative corrections for the non-degenerate zeroth-order case and first-order corrections for the degenerate zeroth-order case.

3. Computational details

In order to characterise the accuracy and performance of the proposed hybrid variational–perturbative approach, we executed pure vibrational ($J = 0$) and rotational–vibrational ($J > 0$) computations for the asymmetric-top C_2H_4 and C_2D_4 as well as the spherical-top CH_4 molecules.

For the computations on C_2H_4 and C_2D_4, the quartic force field of Ref. [30] and atomic masses were employed. The reference structure of D_{2h} symmetry corresponding to this force field has the following structural parameters: $r(\mathrm{CC}) = 1.3371$ Å, $r(\mathrm{CX}) = 1.0832$ Å, and $\alpha(\mathrm{CCX}) = 121.453^\circ$ (X = H or D). The vibrational basis consisted of $6^3 \times 4^9 = 56,623,104$ direct-product Hermite–DVR functions (six functions for the vibrational degrees of freedom with the three lowest harmonic frequencies and four functions for the rest of them) for both the $J = 0$ and 1 computations. To save space, results are reported only for the lowest lying ν_{10}, ν_8, and ν_7 vibrational fundamentals, and for their combinations and overtones.

In case of the CH_4 computations, the octic force field of Ref. [41] was applied. In line with Refs [25] and [42], nuclear masses were used throughout the CH_4 computations. The tetrahedral reference structure corresponding to the force field of Ref. [41] has $r(\mathrm{CH}) = 1.0890$ Å. The vibrational basis consisted of $7^5 \times 6^4 = 21,781,872$ direct-product Hermite–DVR functions (seven and six functions for the bend and the stretch degrees of freedom, respectively) for both the $J = 0$ and $J = 1$–5 computations. For the sake of brevity, we report energy levels corresponding to the bending fundamentals and to their combinations and overtones.

4. Results and discussion

4.1. C_2H_4 and C_2D_4

The hexatomic C_2H_4 molecule was chosen as the first test molecule in order to investigate the accuracy of the hybrid variational–perturbational approach suggested. Table 1 and 2 contain $J = 0$ and $J = 1$ energy levels, respectively, including variational (VAR), zeroth-order (PT_0), and hybrid PT_1 and PT_2 energy levels corresponding to the first- and second-order of perturbation theory, respectively. Due perhaps to the limited basis used in this study, there are three VAR vibrational energy levels (ZPVE, $2\nu_{10}$, and $\nu_7 + \nu_8$ in Table 1) whose absolute deviations from the results published in Ref. [30], employing the same PES and the same masses, are slightly larger than 0.1 cm^{-1}. These discrepancies do not have an effect on the conclusions of this study.

Table 1. Selected $J = 0$ energy levels of C_2H_4, where E and $E^{(0)}$ denote the exact and the zeroth-order variational vibrational energy levels, respectively, while the $E^{(1)}$ and $E^{(2)}$ energy levels are obtained via first- and second-order perturbation theory, respectively. All energy levels reported are referenced to the corresponding zero-point vibrational energies (ZPVE). The force field of Ref. [30] was applied as the potential during the computations.

Vib. label	E (cm^{-1})	$E-E^{(0)}$ (cm^{-1})	$E-E^{(1)}$ (cm^{-1})	$E-E^{(2)}$ (cm^{-1})
ZPVE	11,003.82	5.37	−0.05	−0.02
ν_{10}	821.72	3.56	−0.01	−0.04
ν_8	926.80	8.96	−0.06	−0.09
ν_7	947.22	9.03	−0.06	−0.09
$2\nu_{10}$	1655.88	5.96	0.11	−0.07
$\nu_8 + \nu_{10}$	1751.11	12.43	−0.11	−0.12
$\nu_7 + \nu_{10}$	1775.39	15.02	−0.11	−0.14
$2\nu_8$	1855.78	17.52	−0.20	−0.26
$\nu_7 + \nu_8$	1869.16	17.39	−0.23	−0.22
$2\nu_7$	1895.31	17.90	−0.17	−0.24

The vibrational results of Table 1 show that relative errors of the PT_0 levels do not exceed 1% for the vibrational levels investigated. By adding first-order energy corrections to the PT_0 levels, we get an almost perfect agreement between the PT_1 and VAR vibrational levels, with absolute deviations of the order of 0.1 cm^{-1}. The PT_2 energy corrections, which may be prone to numerical instabilities due to the energy denominators, do not introduce further improvements to the vibrational energy levels examined. Moreover, there are energy levels for which the PT_2 results are slightly worse than their PT_1 counterparts.

The $J = 1$ results given in Table 2 reveal similar trends. It is worth emphasising that the errors of the $J = 1$ PT_0 energy levels are almost exactly the same as those of the corresponding $J = 0$ PT_0 levels. This is due to the choice of the reference Hamiltonian and can be exploited in actual computations.

Similar trends can be observed for the fully deuterated C_2D_4 molecule. By comparing the $J = 0$ (Table 3) and $J = 1$ (Table 4) results obtained for C_2D_4 to those computed for C_2H_4, it becomes evident that both the absolute and the relative errors are considerably lower for C_2D_4. This diminution of errors is due to the larger nuclear mass of D over H and suggests that for even heavier molecules the

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Table 2. Selected $J = 1$ energy levels of C_2H_4, where E and $E^{(0)}$ denote the exact and the zeroth-order variational energy levels, respectively, while the $E^{(1)}$ and $E^{(2)}$ energy levels are obtained via first- and second-order perturbation theory, respectively. All energy levels are referenced to the corresponding ZPVE. The force field of Ref. [30] was applied as the potential during the computations.

Vib. label	E (cm^{-1})	$E-E^{(0)}$ (cm^{-1})	$E-E^{(1)}$ (cm^{-1})	$E-E^{(2)}$ (cm^{-1})
ZPVE	1.81	0.00	0.00	0.00
	5.66	−0.02	−0.02	−0.02
	5.84	−0.02	−0.02	−0.02
ν_{10}	823.52	3.54	−0.03	−0.04
	827.24	3.35	−0.23	−0.05
	827.40	3.33	−0.24	−0.05
ν_8	928.61	8.95	−0.07	−0.09
	932.34	8.79	−0.23	−0.16
	932.50	8.78	−0.24	−0.16
ν_7	949.03	9.02	−0.07	−0.09
	953.04	9.15	0.06	−0.17
	953.21	9.14	0.05	−0.18
$2\nu_{10}$	1657.66	5.93	0.08	−0.08
	1661.32	5.63	−0.22	−0.09
	1661.47	5.61	−0.24	−0.08
$\nu_8+\nu_{10}$	1752.90	12.41	−0.13	−0.13
	1756.51	12.09	−0.45	−0.17
	1756.66	12.07	−0.47	−0.17
$\nu_7+\nu_{10}$	1777.19	15.00	−0.13	−0.15
	1781.03	14.91	−0.22	−0.24
	1781.18	14.89	−0.24	−0.24
$2\nu_8$	1857.59	17.51	−0.21	−0.25
	1861.20	17.22	−0.50	−0.37
	1861.36	17.21	−0.51	−0.38
$\nu_7+\nu_8$	1870.96	17.37	−0.24	−0.23
	1874.83	17.34	−0.28	−0.36
	1874.99	17.33	−0.29	−0.37
$2\nu_7$	1897.12	17.89	−0.18	−0.25
	1901.31	18.18	0.11	−0.38
	1901.47	18.16	0.10	−0.40

Table 3. Selected $J = 0$ energy levels of C_2D_4, where E and $E^{(0)}$ denote the exact and the zeroth-order variational energy levels, respectively, while the $E^{(1)}$ and $E^{(2)}$ energy levels are obtained via first- and second-order perturbation theory, respectively. All energy levels are referenced to the corresponding ZPVE. The force field of Ref. [30] was applied as the potential during the computations.

Vib. label	E (cm^{-1})	$E-E^{(0)}$ (cm^{-1})	$E-E^{(1)}$ (cm^{-1})	$E-E^{(2)}$ (cm^{-1})
ZPVE	8373.69	2.85	−0.02	−0.01
ν_{10}	590.09	2.23	0.00	−0.02
ν_8	719.15	4.87	−0.02	−0.03
ν_7	729.12	4.47	−0.02	−0.03
$2\nu_{10}$	1184.39	4.37	−0.02	−0.02
$\nu_8+\nu_{10}$	1312.41	8.19	−0.04	−0.05
$\nu_7+\nu_{10}$	1320.56	7.86	−0.03	−0.04
$2\nu_8$	1437.34	9.68	−0.07	−0.09
$\nu_7+\nu_8$	1443.66	9.23	−0.09	−0.07
$2\nu_7$	1457.17	8.94	−0.06	−0.08

Table 4. Selected $J = 1$ energy levels of C_2D_4, where E and $E^{(0)}$ denote the exact and the zeroth-order variational energy levels, respectively, while the $E^{(1)}$ and $E^{(2)}$ energy levels are obtained via first- and second-order perturbation theory, respectively. All energy levels are referenced to the corresponding ZPVE. The force field of Ref. [30] was applied as the potential during the computations.

Vib. label	E (cm^{-1})	$E-E^{(0)}$ (cm^{-1})	$E-E^{(1)}$ (cm^{-1})	$E-E^{(2)}$ (cm^{-1})
ZPVE	1.29	0.00	0.00	0.00
	2.99	−0.01	−0.01	−0.01
	3.16	−0.01	−0.01	−0.01
ν_{10}	591.36	2.21	−0.02	−0.02
	593.05	2.18	−0.05	−0.02
	593.21	2.16	−0.07	−0.02
ν_8	720.43	4.86	−0.03	−0.03
	722.17	4.88	−0.01	−0.06
	722.33	4.88	−0.01	−0.06
ν_7	730.42	4.48	−0.01	−0.03
	732.08	4.43	−0.07	−0.05
	732.26	4.44	−0.05	−0.05
$2\nu_{10}$	1185.65	4.35	−0.05	−0.03
	1187.33	4.28	−0.11	−0.03
	1187.47	4.26	−0.13	−0.02
$\nu_8+\nu_{10}$	1313.68	8.17	−0.06	−0.05
	1315.40	8.15	−0.07	−0.08
	1315.55	8.14	−0.09	−0.08
$\nu_7+\nu_{10}$	1321.85	7.85	−0.04	−0.05
	1323.49	7.77	−0.12	−0.07
	1323.66	7.76	−0.12	−0.07
$2\nu_8$	1438.62	9.67	−0.08	−0.10
	1440.39	9.72	−0.03	−0.13
	1440.55	9.71	−0.04	−0.14
$\nu_7+\nu_8$	1444.96	9.24	−0.08	−0.08
	1446.65	9.21	−0.11	−0.14
	1446.83	9.21	−0.10	−0.14
$2\nu_7$	1458.48	8.97	−0.04	−0.08
	1460.11	8.86	−0.14	−0.16
	1460.30	8.88	−0.12	−0.16

errors introduced by the hybrid variational–perturbational approach advocated here will be negligible, especially when one considers the remaining errors of the rovibrational energy levels due to inaccuracies of most practically available PESs.

4.2. CH_4

The pentatomic CH_4 molecule is an ideal example for the case when both the zeroth-order and the variational energy level sets exhibit degeneracies. Table 5 provides $J = 0$ variational (VAR), zeroth- (PT_0), and first-order (PT_1) perturbative energy levels for the vibrational ground state, as well as for the degenerate ν_4 (F_2 symmetry) and ν_2 (E symmetry) bending fundamentals, their overtones, and combinations. Table 6 gives $J = 1$ energy levels for the ground, ν_4, and ν_2 vibrational states. All the energy levels reported are converged to at least 0.01 cm^{-1}.

Table 5. Selected $J = 0$ energy levels of CH_4, where E and $E^{(0)}$ denote the exact and the zeroth-order variational energy levels, respectively, while the $E^{(1)}$ energy levels are obtained via first-order perturbation theory. All energy levels are referenced to the corresponding ZPVE. The symmetry labels correspond to the T_d(M) molecular symmetry group. The force field of Ref. [41] was applied as the potential during the computations.

Vib. label	Symmetry	E (cm^{-1})	$E-E^{(0)}$ (cm^{-1})	$E-E^{(1)}$ (cm^{-1})
(00)(00)	A_1	9691.54	4.55	−0.04
(00)(01)	F_2	1311.74	11.67	−0.05
(00)(10)	E	1533.25	9.05	−0.03
(00)(02)	A_1	2589.75	18.32	−0.25
(00)(02)	F_2	2616.22	25.33	−0.32
(00)(02)	E	2627.28	25.44	−0.17
(00)(11)	F_2	2831.51	21.50	−0.01
(00)(11)	F_1	2846.90	24.60	−0.13
(00)(20)	A_1	3063.47	17.41	0.02
(00)(20)	E	3065.00	18.05	−0.09

The results of Table 5 show that relative errors of the PT_0 levels are less than 1% for all of the vibrational levels examined. After correcting the PT_0 levels according to degenerate first-order perturbation theory, we obtain good agreement between the PT_1 and VAR vibrational levels with absolute errors of the order of 0.1 cm^{-1}, or even less. The same applies to the $J = 1$ PT_0 and PT_1 energy levels reported in Table 6. It is interesting to note that the different $J = 1$ PT_0 degenerate energy level manifolds of the ν_4(E) vibration lie much closer to each other than the corresponding $J = 1$ PT_1 and VAR manifolds.

Besides the $J = 1$ case, this study also investigates rovibrational energy levels with $J = 2 - 5$ for the same vibrational band origins. With the increasing value of J errors of the PT_0 and PT_1 approximations become more pronounced. For the ground and ν_2 vibrational states, PT_1 was found to provide energy levels close to their variational counterparts. In case of the ν_4 bending fundamental, we could identify

Table 6. Selected $J = 1$ energy levels of CH_4, where E and $E^{(0)}$ denote the exact and the zeroth-order variational energy levels, respectively, while the $E^{(1)}$ energy levels are obtained via first-order perturbation theory. All energy levels are referenced to the corresponding ZPVE. The symmetry labels correspond to the T_d(M) molecular symmetry group. The force field of Ref. [41] was applied as the potential during the computations.

Vib. label	Symmetry	E (cm^{-1})	$E-E^{(0)}$ (cm^{-1})	$E-E^{(1)}$ (cm^{-1})
(00)(00)	F_1	10.43	−0.02	−0.02
(00)(01)	A_2	1312.41	1.85	−0.17
	F_2	1317.25	6.69	−0.16
	F_1	1326.73	16.16	−0.41
	E	1327.03	16.44	−0.13
(00)(10)	F_2	1543.79	9.11	0.03
	F_1	1543.91	9.22	0.14

Table 7. $J = 2$ energy levels of CH_4 for the ν_4 bending fundamental. E and $E^{(0)}$ denote the exact and the zeroth-order variational energy levels, respectively, while the $E^{(1)}$ energy levels are obtained via first-order perturbation theory. All energy levels are referenced to the corresponding ZPVE. The symmetry labels correspond to the T_d(M) molecular symmetry group. The force field of Ref. [41] was applied as the potential during the computations.

Symmetry	E (cm^{-1})	$E-E^{(0)}$ (cm^{-1})	$E-E^{(1)}$ (cm^{-1})
F_2	1328.29	−3.22	−13.52
E	1337.78	6.28	−0.58
F_2	1338.04	6.46	−11.51
A_1	1351.54	20.02	−1.40
F_1	1352.17	20.58	9.49
F_1	1352.65	21.05	13.58

PT_0 rovibrational level pairs for which the corresponding W^0_{ij} coupling matrix elements are substantial. As the W^0_{ij} matrix elements between the different energy level manifolds are not taken into account by PT_1, the accuracy of PT_1 deteriorates and in some cases PT_1 can perform even worse than PT_0. Two such problematic $J = 2$ level pairs of F_2 and F_1 symmetries are given in Table 7. While in these cases PT_2 could be expected to improve upon the PT_1 results, if the PT_0 rovibrational levels are close to each other PT_2 can break down. In such cases, one must be careful with the hybrid approach advocated here.

5. Summary

To the best of our knowledge, the version of DEWE developed as part of the present study is the first rovibrational nuclear motion code based on the Eckart–Watson Hamiltonian which (1) employs a DVR, (2) treats the μ tensor in an exact fashion, i.e., without truncation, and (3) is capable of a first- and second-order perturbative treatment of the Coriolis coupling terms of the kinetic energy operator.

Based on a thorough analysis of the computed vibrational and rotational–vibrational energy levels of the hexatomic C_2H_4 and C_2D_4 molecules and of the pentatomic CH_4 molecule, we can make the following observations about the hybrid variational–perturbational nuclear motion algorithm: (1) The first-order perturbational treatment of the Coriolis coupling terms of the Eckart–Watson Hamiltonian performs extremely well for many of the rotational–vibrational energy levels computed for the three semi-rigid molecules. (2) If different PT_0 energy level manifolds are coupled by substantial W^0_{ij} matrix elements, the accuracy of PT_1 can be reduced substantially. (3) The effect of the second-order perturbative energy corrections on the rotational–vibrational levels is almost negligible and thus not worth computing if there are no significant W^0_{ij} matrix elements. (4) As to the effectiveness of the proposed variational–perturbational approach, the hybrid treatment

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can reduce the cost of certain parts of the computations by almost an order of magnitude.

Based on these observations, the perturbative treatment of the Coriolis coupling terms of the Eckart–Watson Hamiltonian is recommended as a relatively inexpensive and still accurate alternative to the full variational treatment based on the same Hamiltonian. The hybrid approach is especially recommended for larger and heavier semi-rigid molecules, whose detailed studies are envisioned in the near future.

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