**REGULAR ARTICLE**

# An equation of motion approach for the vibrational transition energies in the effective harmonic oscillator formalism: the Random phase approximation

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**Abstract.** A theory for calculating vibrational energy levels and infrared intensities is developed in the equation of motion framework at the random phase approximation level. The vibrational Hamiltonian is expanded in the harmonic oscillator ladder operators making a Hamiltonian a bosonic Hamiltonian. The excitation operator is expanded to include at most two creations and two annihilation operators making it equivalent to the random phase approximation. The method is applied for the calculation of vibrational spectral properties of two molecules. The results are found to be satisfactory, making this approach a viable option for large molecular systems.

**Keywords.** Bosons; RPA; molecular vibrations; IR spectroscopy.

## 1. Introduction

Infrared (IR) spectroscopy is one of the standard methods for the characterization of molecules.[1] More generally both IR and Raman spectroscopy techniques provide information regarding the vibrational energy levels and their transition moment integrals, that can be used to get an understanding of the overall molecular structure and dissociation energies. However, such an analysis requires a theoretical understanding of the vibrational eigenstates of the concerned molecule. With this motivation, several approaches have been developed to solve the vibrational problem over the past several years.

The standard approach for the computational vibrational spectroscopy starts from the Born–Oppenheimer approximation. The total molecular wavefunction, in the molecular center of mass frame, is decomposed as the product of nuclear coordinate dependent electronic wavefunction and nuclear wavefunction. The electronic wavefunction is obtained as the eigenfunction of the (nuclear coordinate dependent) electronic Hamiltonian. The resultant eigenvalues also depends on the nuclear coordinates and become the potential energy functions in the nuclear Schrödinger equation. The solution of the resultant nuclear Schrödinger equation provides the energies of the molecular rovibrational eigenstates.

There are several coordinate systems in which the nuclear Hamiltonian can be expanded. The most convenient coordinate system uses the cartesian normal coordinates. Watson[2] derived the vibrational Hamiltonian in terms of the such normal coordinates. It is given as

$$H = \sum_i P_i^2/2 + V(q) + V_W + V_C .$$ (1)

Here, $q_i$ are the mass-weighted normal coordinates, $P_i$ are the corresponding conjugate momenta, $V_W$ is Watson mass-dependent term and $V_C$ is Coriolis coupling term. The potential energy surface (PES) derived from the electronic structure calculations becomes the potential energy function, $V(q)$, for the vibrational calculation. In principle, this function is an infinite series in terms of the normal coordinates. For practical application it is truncated at the fourth power. Within this quartic approximation, the potential energy function is written as

$$V(q) = 1/2 \sum_i f_{ii} q_i^2 + \sum_{i \le j \le k} f_{ijk} q_i q_j q_k + \sum_{i \le j \le k \le l} f_{ijkl} q_i q_j q_k q_l.$$ (2)

Here, $f_{ii}$ are the squares of the harmonic frequencies of the normal modes $q_i$, $f_{ijk}$ and $f_{ijkl}$ are the cubic and quartic anharmonic coupling constants, respectively. Given the presence of anharmonic terms in the Hamiltonian, the vibrational Schrödinger equation is not analytically solvable. Several efforts have been reported in the literature for solving it. Prominent among them are the vibrational self consistent field (VSCF) approximation,[3–7] vibrational configuration interaction (VCI),[8–13] vibrational perturbation theory (VPT)[14–19] and vibrational coupled cluster method (VCCM).[20–37] One method which received relatively little attention is the effective harmonic oscillator(EHO) approximation.[38–42] In this approach, the wavefunction of the anharmonic molecular vibrations are approximated by the eigenfunction of an EHO.[38] The harmonic oscillator wavefunctions in one dimension are characterized by two parameters, the frequency of the oscillator and the location of the centroid of the wavefunction. These two parameters are treated as variational parameters to obtain the optimized harmonic oscillator eigenfunctions for a given state of a real molecule. Computational studies have shown that such an EHO approximation provides vibrational transition energies within a few wavenumbers of the vibrational SCF approximation[38] with much less computational effort. Since only two parameters are varied for each degree of freedom, the computational resources needed for the EHO are quite small compared to the VSCF approach. Consequently, the method is amenable to applications for quite large molecules.

Notwithstanding the numerical performance of the EHO, it has a few limitations. The eigenvalues of EHO are subject to variational collapse[43] in some cases. A second limitation is that separate computations have to be done for each state, the transition energies being obtained as the differences of the state energies. Since the state energies are quite large, the transition energies suffer from rounding off errors. In addition all the states in the relevant energy range have to be calculated explicitly. The number of such states increases exponentially with the number of vibrational modes. It would be desirable to develop approximations which scale more mildly with the number of degrees of freedom and compute the transition energies directly rather than compute them as differences of two large numbers.

One such method is the equation of motion approach (EOM).[44,45] In this approach one defines an excitation operator that maps the ground state wavefunction to an excited state wavefunction. It is possible to show that the commutator of this excitation operator with the Hamiltonian, acting on the ground state gives the transition energies directly. It is necessary to make approximations to the excitation operator and the ground state for practical calculations. Several approximations have been developed and studied for nuclear, molecular and solid state systems.[46–54] The simplest approximation in the EOM approach is to use the Hartree-Fock approximation for the ground state and expand the excitation operator in terms of single hole-particle excitation and de-excitation operators. This approximation is called the random phase approximation (RPA). It has been applied extensively for obtaining the transition energies of nuclei and molecular electronic systems.[47–53]

While the RPA has been applied extensively for fermionic systems, relatively few applications have been made to bosonic systems.[55] Most of these studies however have been confined to the determination of the ground state energies rather than transition energies. The goal of the present work is to develop and study the utility of the RPA within the EHO framework for the description of molecular vibrations. The requisite theory is reviewed in section 2. We present some model applications in section 3, that provide an insight in to the utility of the RPA for the description of molecular vibrations. Finally section 4 contains a few concluding remarks.

## 2. Theory

The EOM method for the transition energies requires two components. The first is the ground state wavefunction, $|\Psi_g\rangle$. The second is the excitation operator, $X_e^\dagger$, which maps the ground state wavefunction to an excited state wavefunction.

$$|\Psi_e\rangle = X_e^\dagger|\Psi_g\rangle . \tag{3}$$

The excitation operator satisfies the equation of motion

$$[H, X_e^\dagger]|\Psi_g\rangle = \Delta E_e X_e^\dagger|\Psi_g\rangle , \tag{4}$$

where, $\Delta E_e$ is the transition energy $E_e - E_g$. Equation 4 is the starting point in making approximations for practical applications. Approximations have to be made separately to the ground state wavefunction and the excitation operator.

We first start with the ground state calculation. In the spirit of EHO formalism we posit a trail wavefunction

$$|\Psi_t\rangle = \prod_\alpha exp[-\omega_\alpha(q_\alpha - q_\alpha^0)^2/2]. \tag{5}$$

The parameters $\omega_\alpha$ and $q_\alpha^0$ are determined by minimizing the energy functional with respect to them. The resulting working equations for $\omega_\alpha$ and $q_\alpha^0$ are[27]

$$q_\alpha^0 = -\left[\sum_{\beta \leq \gamma} f_{\alpha\beta\gamma}q_\beta^0 q_\gamma^0 + \sum_{\beta \leq \gamma \leq \delta} f_{\alpha\beta\gamma\delta}q_\beta^0 q_\gamma^0 q_\delta^0 \right. $$
$$\left. + \sum_\beta f_{\alpha\beta\beta}/2\omega_\beta + \sum_{\beta\gamma} f_{\alpha\beta\beta\gamma}q_\gamma^0/2\omega_\beta\right]/2f_{\alpha\alpha}, \tag{6}$$

$$\omega_\alpha = \left[2\left(f_{\alpha\alpha} + \sum_\beta f_{\alpha\alpha\beta}q_\beta^0 + \sum_\beta f_{\alpha\alpha\beta\beta}/2w_\beta \right.\right.$$
$$\left.\left. + \sum_{\beta \leq \gamma} f_{\alpha\alpha\beta\gamma}q_\beta^0 q_\gamma^0\right)\right]^{1/2}. \tag{7}$$

The trial wave function 5, with the parameters $\omega_\alpha$ and $q_\alpha^0$ frozen at the roots of Eqs. (6, 7) now becomes the ground state $|\Psi_g\rangle$ within this approximation. We next define the harmonic oscillator ladder operators,

$$a_\alpha = \left(q_\alpha - q_\alpha^0 + \frac{\partial}{\omega_\alpha\partial q_\alpha}\right)\sqrt{\omega_\alpha/2}, \tag{8}$$

$$a_\alpha^\dagger = \left(q_\alpha - q_\alpha^0 - \frac{\partial}{\omega_\alpha\partial q_\alpha}\right)\sqrt{\omega_\alpha/2}. \tag{9}$$

The Hamiltonian is expressed in terms of these ladder operators. The optimized EHO ground state $|\Psi_g\rangle$ satisfies

$$a_\alpha|\Psi_g\rangle = 0. \tag{10}$$

on the ground state wave function. Given this property, $|\Psi_g\rangle$ becomes the vacuum state in the Fock space of the multi dimensional harmonic oscillator.

We next turn to the construction of the excitation operator. In the spirit of the RPA we define the excitation operator as

$$X^\dagger = \sum_\alpha Y_\alpha^1 a_\alpha^\dagger + \sum_{\alpha\beta} Y_{\alpha\beta}^2 a_\alpha^\dagger a_\beta^\dagger$$
$$+ \sum_\alpha Z_\alpha^1 a_\alpha + \sum_{\alpha\beta} Z_{\alpha\beta}^2 a_\alpha a_\beta. \tag{11}$$

The hermitian adjoint of the excitation operator also satisfies what is termed as vacuum annihilation condition or killer condition[56,57] similar to Eq. 10. Since the ground state cannot be de-excited further, we require

$$X|\Psi_g\rangle = 0. \tag{12}$$

Substitution of ansatz 11 in Eq. 4 leads to the final working equation for the transition energies and the excitation operator components

$$\begin{bmatrix} A^{11} & A^{12} & B^{11} & B^{12} \\ A^{21} & A^{22} & B^{21} & B^{22} \\ -B^{11} & -B^{12} & -A^{11} & -A^{12} \\ -B^{21} & -B^{22} & -A^{21} & -A^{22} \end{bmatrix} \begin{bmatrix} Y^1 \\ Y^2 \\ Z^1 \\ Z^2 \end{bmatrix} = \Delta E \begin{bmatrix} Y^1 \\ Y^2 \\ Z^1 \\ Z^2 \end{bmatrix} \tag{13}$$

The individual elements of the sub matrices are

$$A_{\alpha,\beta}^{11} = \omega_\alpha\delta_{\alpha\beta}, \tag{14}$$

$$A_{\alpha,\beta\gamma}^{12} = A_{\beta\gamma,\alpha}^{21} = g_{12}f_{\alpha\beta\gamma}/\sqrt{3\omega_\alpha\omega_\beta\omega_\gamma}, \tag{15}$$

$$A_{\alpha\beta,\gamma\delta}^{22} = (\omega_\alpha + \omega_\beta)\delta_{\alpha\gamma}\delta_{\beta\delta}$$
$$+ f_{\alpha\beta\gamma\delta}g_{22}/\sqrt{16\omega_\alpha\omega_\beta\omega_\gamma\omega_\delta}, \tag{16}$$

$$B_{\alpha,\beta\gamma}^{12} = B_{\beta\gamma,\alpha}^{21} = g_{03}f_{\alpha\beta\gamma}/\sqrt{8\omega_\alpha\omega_\beta\omega_\gamma}, \tag{17}$$

$$B_{\alpha\beta,\gamma\delta}^{22} = g_{04}f_{\alpha\beta\gamma\delta}/\sqrt{16\omega_\alpha\omega_\beta\omega_\gamma\omega_\delta}. \tag{18}$$

Here $g_{ij}$ are the combinatorial factors that come when two sets of boson operators are contracted.

The eigenvectors of the RPA matrix defined in Eq. 13 should not be normalized in the conventional fashion. The wavefunction of the excited state is given by

$$|\Psi_e\rangle = \sum_\alpha Y_\alpha^1|\alpha_1\rangle + \sum_{\alpha\beta} Y_{\alpha\beta}^2|\alpha_1\beta_1\rangle, \tag{19}$$

because the de-excitation operators gives zero when acting on the vacuum. Here $\alpha$ and $\beta$ represent the vibrational modes that are excited to their fundamental states. Thus, their influence is completely ignored in the excited state wavefunction, and thus on the norm of it. Instead, in the spirit of the EOM[44] approach we define norm of the excited state as

$$\langle\Psi_e|\Psi_e\rangle = \langle\Psi_g|X_e, X_e^\dagger|\Psi_g\rangle$$
$$= \langle\Psi_g|[X_e, X_e^\dagger]|\Psi_g\rangle$$
$$= \sum_\alpha Y_\alpha^1 Y_\alpha^1 + \sum_{\alpha\beta} Y_{\alpha\beta}^2 Y_{\alpha\beta}^2(1 + \delta_{\alpha\beta})$$
$$- \sum_\alpha Z_\alpha^1 Z_\alpha^1 - \sum_{\alpha\beta} Z_{\alpha\beta}^2 Z_{\alpha\beta}^2(1 + \delta_{\alpha\beta}) \tag{20}$$

Here, we have invoked the killer condition, Eq. 12, in the second step. We normalize the excited states with

this norm. In the same spirit, the transition matrix elements are obtained from

$$\langle\Psi_e|d|\Psi_g\rangle = \langle\Psi_g|X_e d|\Psi_g\rangle$$
$$= \langle\Psi_g|[X_e, d]|\Psi_g\rangle. \tag{21}$$

Assuming a linear dipole operator,

$$d = \sum_\alpha d_\alpha(a_\alpha + a_\alpha^\dagger) \tag{22}$$

$$\langle\Psi_e|d|\Psi_g\rangle = \sum_\alpha [Y_\alpha^1 d_\alpha - Z_\alpha^1 d_\alpha] \tag{23}$$

With this, the integrated band strength of an IR transition is given by[31]

$$A(\omega) = 2.509\omega\langle\Psi_g|[d, X^\dagger]|\Psi_g\rangle\langle\Psi_g|[X, d]|\Psi_g\rangle$$
$$= 2.509\omega\left[\sum_\alpha d_\alpha(Y_\alpha^1 - Z_\alpha^1)\right]^2. \tag{24}$$

Here, $\omega$ is the transition energy in wave numbers, and the dipole matrix elements are in atomic units. The band strength is in km.mol$^{-1}$.

Equations 13–24 are the working equations we have used in calculating the vibrational spectra.

## 3. Results and Discussion

We have implemented the calculation of the vibrational energy levels and spectral intensities described in the previous section. We present the results of the calculations of two molecules, $H_2O$ and ethylene.

Water is a quintessential local mode molecule. The large mass of the central atom coupled with the high anharmonicity of OH stretches makes it a stringent test for the applicability of any method. The quartic potential energy surface for $H_2O$ was obtained from Gaussian 09 program[58] using B3LYP method with a cc-pVTZ basis set. The RPA results are compared with $\Delta$EHO, $\Delta$VSCF, VCCM and converged VCI results. The VSCF and VCI calculations were carried out with 8, 16 and 8 harmonic oscillator eigenfunctions for the three vibrational modes respectively. The transition

energies for the three fundamental transitions are presented in Table 1. As can be inferred from the data in Table 1, the RPA gives the second best results among the four, while the VCCM approach gives the best results. The VCCM calculations were made with the cluster operator and the excitation operator truncated at the four boson level. As has been shown earlier,[28,29] this level of approximation is highly accurate. The RPA with only two boson excitation operators cannot be expected to match it. On the other hand it outperforms $\Delta$EHO and $\Delta$VSCF significantly. We have calculated the standard deviation ($\sigma$) of the results of these methods with respect to the full CI results. These values are also presented in Table 1. The $\Delta$EHO method which retains the harmonic oscillator character of the excited states and RPA are formally of similar level of approximation. On the average the RPA deviates from the converged VCI results by about 12 cm$^{-1}$, while the $\Delta$EHO and $\Delta$VSCF deviate from the VCI results by as much as about 50 cm$^{-1}$. This suggests that the inclusion of the annihilation operators in the RPA excitation operator provides a better balance of the relaxation and changes in the correlation energy during the excitation process than the $\Delta$EHO and $\Delta$VSCF approaches. Next, we summarize the integrated band strengths by RPA and VCCM methods in Table 2. Again as can be seen, the RPA provides a fairly good approximation to the near exact VCCM results. A curious feature that we noticed is that the RPA systematically underestimates the integrated band strengths compared to the VCCM intensities. We could not find any technical reason for this observation.

We next move on to the second of our test molecules, ethylene. The quartic potential energy surface for it was obtained from Gaussian 09 program[58] using B3LYP method with a 6-311++G(2d,2p) basis set. The transition energies for this by various methods are presented in Table 3 along with the standard deviation of each approximation with respect to the VCCM results. We were unable to carry out VCI calculations for this 12 mode system. However, we have included the experimental frequencies[59] for comparison. The VSCF calculations were carried out with 8 harmonic

**Table 1.** Transition energies of (in cm$^{-1}$) $H_2O$.

| Modes | RPA | VCCM | $\Delta$EHO | $\Delta$ VSCF | VCI |
|---|---|---|---|---|---|
| $1_1$ | 3655 | 3674 | 3761 | 3762 | 3675 |
| $2_1$ | 1570 | 1566 | 1566 | 1570 | 1566 |
| $3_1$ | 3751 | 3752 | 3778 | 3788 | 3755 |
| $\sigma$ | 12 | 1.82 | 51.39 | 53.77 | – |

**Table 2.** Integrated band strengths of fundamental transitions (in km mol$^{-1}$) of $H_2O$.

| Modes | RPA | VCCM |
|---|---|---|
| $1_1$ | 3.11 | 3.29 |
| $2_1$ | 68.78 | 72.28 |
| $3_1$ | 38.82 | 41.53 |

**Table 3.** Transition energies of ethylene (in $cm^{-1}$).

| Modes | RPA | VCCM | ΔEHO | ΔVSCF | Exp[a] |
|---|---|---|---|---|---|
| $1_1$ | 2987.3 | 2993.6 | 3037.3 | 3048.8 | 3026 |
| $2_1$ | 1646.5 | 1637.5 | 1658.6 | 1660.3 | 1623 |
| $3_1$ | 1353.8 | 1352.4 | 1364.9 | 1365.1 | 1342 |
| $4_1$ | 1027.2 | 1023.6 | 1049.2 | 1049.1 | 1023 |
| $5_1$ | 2981.9 | 2963.9 | 3022.8 | 3022.9 | 2989 |
| $6_1$ | 1441.2 | 1437.3 | 1457.8 | 1457.7 | 1444 |
| $7_1$ | 951.9 | 947.8 | 976.4 | 976.2 | 943 |
| $8_1$ | 3085.6 | 3065.7 | 3107.2 | 3107.3 | 3106 |
| $9_1$ | 830.5 | 825.9 | 855.2 | 854.9 | 826 |
| $10_1$ | 3067.7 | 3044.4 | 3077.5 | 3077.6 | 3103 |
| $11_1$ | 1221.2 | 1218.4 | 1235.8 | 1235.8 | 1236 |
| $12_1$ | 948.8 | 944.2 | 974.8 | 974.6 | 949 |
| σ | 11.3 | – | 32.54 | 34.12 | – |

[a]Ref. [59]

oscillator eigenfunctions for each mode. The trends noticed in $H_2O$ are present in this system also, with RPA transition energies being closer to the VCCM values than ΔEHO and ΔVSCF as can be seen from the standard deviation values of different approaches from the VCCM values. We have not compared the computational results with experiment directly, since the errors in them are not only from the approximations invoked in the vibrational calculations, but also due to the inherent approximations in the PES. However, in this particular case, RPA is generally closer to the experimental value also than EHO and VSCF. Table 4 contains the integrated band strengths of the fundamental transitions of ethylene. For all its lack of technical sophistication, the RPA is nearly as accurate as the more sophisticated VCCM approach. In these two molecules, and others that we have calculated, we found similar trends.

We would like to make some comments on a curious observations we made in the results presented in Table 3. The ΔEHO and ΔVSCF results are very close to each other, often within 1 $cm^{-1}$. In principle, the two approximations are different. The intra mode anharmonicity is exactly treated in the VSCF approach. It is treated only approximately by the EHO. For example the cubic term is approximated as

**Table 4.** Integrated band strengths of fundamental transitions (in km mol$^{-1}$) of ethylene.

| Modes | RPA | VCCM |
|---|---|---|
| $5_1$ | 13.12 | 14.02 |
| $6_1$ | 9.80 | 10.42 |
| $8_1$ | 19.38 | 20.76 |
| $9_1$ | 0.17 | 0.14 |
| $12_1$ | 98.26 | 104.97 |

$$q^3 \approx 3q^2\langle q \rangle + 3q\langle q^2 \rangle \tag{25}$$

The VSCF Fock matrix has a non zero matrix element between states $|n\rangle$ and $|n+3\rangle$. The EHO does not have a similar matrix element. This has an effect on the overall eigenvalues by the two approaches. However, this difference appears to be nearly a constant, since, given the relatively large energy gap between $|n\rangle$ and $|n+3\rangle$, these states mix little. A similar argument holds for the $q^4$ terms as well. We believe this is the reason for the observed near equal values of ΔEHO and ΔVSCF approaches. The effect is particularly noticeable in non-totally symmetric modes which do not have intra mode cubic potential terms. The quartic terms, which are often very small, cannot produce a significant difference between these two approaches.

## 4. Conclusions

We have explored the possibilities of using the random phase approximation for the description of vibrational spectra in this work. We have calculated both the transition energies and infrared spectral intensities by this approach. Since the excitation operator is truncated at a low order, and the ground state is approximated as an optimized HO ground state, the method cannot be expected to describe overtone and combination bands. The frequencies and intensities for the fundamental transitions were fairly good. This gives rise to the hope that if the excitation operator is extended up to, perhaps, four boson operators and the ground state description is improved beyond the EHO by the inclusion of a first order or second order perturbative corrections to the ground state over and above the EHO, the method might perform well enough to provide a satisfactory description of the low energy part (below 4000 $cm^{-1}$) of the vibrational spectra. However, a judicious balance must be stuck in the definition of the excitation operator and the ground state description. Such an attempt faces two difficulties. The RPA like methods diagonalize the Hamiltonian matrix in the operator space in the final step. In case of RPA, the dimension of the matrix is of the order of $N^2$, where N is the number of vibrational modes. Extending the excitation operator to a four boson excitation operator requires a matrix of the order of about $N^4/12$. Even for ethylene, a relatively small molecule it would mean that the matrix size increases from 144 to about 1800. The resulting matrix diagonalization would require a much larger memory and CPU time. Second, the choice of the ground state

ansatz that is well matched with the excitation operator would require some detailed explorations. RPA itself seems to have such balance. Explorations must be made to develop such balanced description in extended RPA like approximations. Efforts in this direction are going on in our group and would be reported in due course.

RPA has a long history in many-body physics. It is a common approximation reached through several approaches. The polarization propagator, the EOM, the small amplitude time dependent HF approximation give RPA at the lowest level of approximations. It satisfies the Thomas-Reichie-Kuhn sum rule.[44,60] It is also related to the stability of the ground state wavefunction. If the RPA matrix has complex eigenvalues, it indicates that the ground state wavefunction used is not the global minimum in the parameter space. This is the equivalent of the Thouless stability condition[61] for the many fermions systems. Its performance for the vibrational systems, an application to particle number non-conserving bosonic Hamiltonians is perhaps the validation of its formal strength.

## Acknowledgements

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