Abstract

In this Letter we extend the perturbed matrix method by explicitly including the nuclear degrees of freedom and showing how to treat a non-homogeneous electric field. In a previous Letter we showed that this method provides reliable perturbed energies. In the present Letter we evaluate a more sophisticated property such as molecular polarizability for a water molecule.

1. Introduction

Recently we developed a theoretical method, the perturbed matrix method (PMM), for modeling perturbed molecular eigenstates [1], which proved to be promising at least for the set of molecules studied. In the PMM instead of including directly in the Hamiltonian operator the perturbation term, as usual for Hartree–Fock based calculations, the effect of the perturbation is obtained diagonalizing the perturbed Hamiltonian matrix constructed in the basis set of the unperturbed Hamiltonian eigenstates. In the previous Letter we introduced the method considering homogeneous perturbing (electric) fields and pure electronic eigenfunctions, i.e., molecular geometry was fixed. In this Letter we explicitly explain how to include nuclear degrees of freedom (dof) in the calculations and to treat non-homogeneous perturbing fields. Such an extension of the method could be of great importance for treating electronic properties of molecules in condensed phase, where molecular interactions cannot be always well approximated by homogeneous fields, and to obtain a reliable evaluation of the molecular properties in complex systems where the coupling between the perturbation and nuclear and electronic dof can be relevant. The Letter is organized as follows: in Section 2 we illustrate the basic equations of PMM, generalized for non-homogeneous fields; in Section 3 we derive from first
principles how to couple electronic and nuclear dof in order to obtain a compact mathematical description; in Section 4 we show how the theoretical results of the previous sections can be used to obtain molecular polarizability for a given electronic state and finally, in the last section, we apply and test the method evaluating the polarizability in the ground and first electronic excited states of a water molecule.

2. Basic derivations

The time independent Schroedinger’s equation, in matrix notation, for a perturbed system is

$$\tilde{H}c_i = \mathcal{H}_i c_i,$$  \hspace{1cm} (1)

where $\tilde{H} = \tilde{H}^0 + \tilde{V}$, $c_i$ is the $i$th eigenvector of the perturbed Hamiltonian matrix $\tilde{H}$, $\mathcal{H}_i$ the corresponding Hamiltonian eigenvalue, $\tilde{H}^0$ is the unperturbed Hamiltonian matrix and $\tilde{V}$ is the perturbation energy matrix. The Hamiltonian matrix and its eigenvectors can be expressed in the basis set defined by the unperturbed Hamiltonian matrix eigenvectors, and hence the element of the Hamiltonian matrix is

$$H_{l,p} = \langle \phi^0_l | \mathcal{H} | \phi^0_p \rangle = \mathcal{H}^0_{l,p} \delta_{l,p} + \langle \phi^0_l | \tilde{V} | \phi^0_p \rangle,$$  \hspace{1cm} (2)

where $\phi^0_l$ is the $l$th eigenfunction of the unperturbed Hamiltonian operator, $\mathcal{H}^0_{l,p}$ the corresponding eigenvalue, $\delta_{l,p}$ Kroenecker’s delta and $\tilde{V}$ is the perturbation energy operator. From the above equations it is evident that for obtaining the eigenvectors and eigenvalues, and hence every property, of the perturbed Hamiltonian eigenstates, we only have to diagonalize the matrix $\tilde{H}$, as given by Eq. (2). For a system interacting with an external electric field, we can express in general the perturbation operator in Eq. (2) in terms of the electric potential $\mathcal{V}$ as

$$\mathcal{V} = \sum_j q_j \mathcal{V}(r_j)$$  \hspace{1cm} (3)

with $r_j$ the coordinates of the $j$th charged particle and $q_j$ the corresponding charge. Expanding at the second order $\mathcal{V}$ around a given position $r_0$ we have

$$\mathcal{V}(r_j) \approx \mathcal{V}(r_0) - \sum_{k=1}^3 E_k (r_{jk} - r_{0k})$$

$$- \frac{1}{2} \sum_{k=1}^3 \sum_{k'=1}^3 \left( \frac{\partial^2 E_k}{\partial r_{k'}^2} \right)_{r=r_0} (r_{jk} - r_{0k})(r_{jk'} - r_{0k'})$$

$$E_k = -\left( \frac{\partial \mathcal{V}}{\partial r_{jk}} \right)_{r=r_0} = -\left( \frac{\partial \mathcal{V}}{\partial r_k} \right)_{r=r_0},$$

where $k$ and $k'$ define the three components of a vector in space and $r$ is the generic position vector. From these equations, defining with $q_T$ the total charge, we readily obtain

$$\langle \phi^0_l | \tilde{V} | \phi^0_p \rangle \approx q_T \mathcal{V}(r_0) \delta_{l,p} - E \cdot \langle \phi^0_l | \mathbf{\mu} | \phi^0_p \rangle$$

$$+ \frac{1}{2} \text{Tr} [\mathbf{\Theta} \tilde{Q}_{l,p}],$$  \hspace{1cm} (4)

$$\tilde{Q}_{l,p} = \left[ \tilde{Q}_{l,p} \right]_{k,k'}$$

$$= \sum_j q_j \langle \phi^0_l | (r_{jk} - r_{0k})(r_{jk'} - r_{0k'}) | \phi^0_p \rangle,$$  \hspace{1cm} (5)

where

$$\mathbf{\Theta}_{k,k'} = -\left( \frac{\partial E_k}{\partial r_{k'}} \right)_{r=r_0},$$  \hspace{1cm} (6)

$$\mathbf{\mu} = \sum_j q_j (r_j - r_0).$$  \hspace{1cm} (7)

Hence the complete perturbed Hamiltonian matrix is

$$\tilde{H} = \tilde{H}^0 + \mathbf{i} q_T \mathcal{V} + \mathbf{\tilde{Z}}(\mathbf{E})$$  \hspace{1cm} (8)

$$\left[ \mathbf{\tilde{Z}}_1 \right]_{l,p} = -E \cdot \langle \phi^0_l | \mathbf{\mu} | \phi^0_p \rangle,$$  \hspace{1cm} (9)

$$\left[ \mathbf{\tilde{Z}}_2 \right]_{l,p} = \frac{1}{2} \text{Tr} [\mathbf{\Theta} \tilde{Q}_{l,p}],$$  \hspace{1cm} (10)

From the last equations it is evident that a second order expansion of the electric potential, able to describe electric fields up to linear behavior over the molecular size, requires the knowledge of the total charge and the unperturbed dipoles and quadrupoles. Higher order expansions can be in principle worked out in the same way but would require information on higher order multipoles which are typically very difficult to obtain. More-
over, it is rather unusual that an applied electric field is beyond the linear approximation over a molecular size. Note that for uncharged systems and homogeneous applied fields, i.e., Θ is a zero elements matrix, Eq. (8) reduces to the one given in the previous Letter [1]. The above equations are very general and could be used to describe either a perturbed Born–Oppenheimer (BO) surface, i.e., \( \Phi^0_l \) corresponding to the \( l \)th unperturbed electronic eigenstate for a fixed nuclear position, as well as perturbed complete quantum mechanical eigenstates including nuclear dof. However, in the next subsection we show that it is very convenient to use the above equations to evaluate the perturbed energy on the BO surfaces, and then to include the possible nuclear quantum dof.

3. Combining electronic and nuclear degrees of freedom

In this Letter we show that it is rather simple to use perturbed BO surfaces, corresponding to different electronic eigenstates, to include also nuclear dof in PMM calculations, at least within local harmonic approximations on the BO surfaces, i.e., harmonic quantum nuclear motions. Typically in quantum chemistry coupling between nuclear and electronic dof is achieved either by considering all nuclear dof in the BO approximation, or treating all of them as quantum vibrating coordinates, in the latter case using also anharmonic corrections [2,3]. In our approach we distinguish between classical and quantum nuclear dof approximating the Hamiltonian eigenstates, for a single molecule, as the product of an electronic eigenfunction \( \Phi(x, \xi, \beta_0) \) with two nuclear wave functions, \( \phi_c(\beta) \) and \( \phi_d(\xi) \) describing the quantum vibrational and classical nuclear dof, respectively. In the previous wave functions \( x \) are the electronic coordinates and \( \xi, \beta \) the nuclear classical and quantum coordinates respectively, and \( \Phi \) is evaluated on the BO surface position \( \xi, \beta_0 \) corresponding to the energy minimum at fixed classical nuclear coordinates. In this Letter we always assume that for fixed \( \xi \) we only have a single energy minimum in \( \beta \) for every BO surface. Note also that \( \phi_d \) is fully confined within a phase space differential volume and so it acts fixing the classical nuclear coordinates and conjugated momenta to a phase space point. We can define the total molecular Hamiltonian as \( \hat{H} = \hat{H}^\text{BO}(x, \pi_x, \xi, \beta) + \hat{K}(\xi, \beta, \pi_\xi, \pi_\beta) \) with \( \hat{H}^\text{BO} \) the BO surface Hamiltonian operator (including the pure electronic Hamiltonian, the electron–nuclei interaction and the nuclear–nuclear interaction) and \( \hat{K} \) the nuclear kinetic energy operator, and \( \pi_x, \pi_\xi, \pi_\beta \) are the electrons and nuclear conjugated momenta operators (note that we explicitly show the conjugated momenta associated to the classical and quantum coordinates). Hence, we have for a given \( l \)th BO surface (\( l \)th electronic eigenstate)

\[
\langle \phi_{cl} \Phi_l | \hat{H} | \phi_{cl} \rangle_{\phi_{cl}, l} = \langle \phi_{cl} \Phi_l | \hat{H}^\text{BO} | \phi_{cl} \rangle_{\phi_{cl}, l} + \langle \phi_{cl} \Phi_l | \hat{K} | \phi_{cl} \rangle_{\phi_{cl}, l}
\]

\[
= \mathcal{U}_l(\xi) \phi_{cl, l}, \quad (11)
\]

where \( \mathcal{U}_l(\xi) \) is the Hamiltonian eigenvalue, including the quantum nuclear vibration, for a given position of the classical nuclear coordinates on the \( l \)th BO surface. If in the last equation we consider a second order expansion around the minimum energy position, for \( \hat{H}^\text{BO} \) in terms of \( \beta \), we obtain

\[
\mathcal{U}_l(\xi) \phi_{cl, l} = \left( \mathcal{U}_l^\text{BO} + \Delta \beta^T \frac{\bf{A}}{2} \Delta \beta \right) \phi_{cl, l} + \langle \phi_{cl} \Phi_l | \hat{K} | \phi_{cl} \rangle_{\phi_{cl}, l}, \quad (12)
\]

\[
A_{ij}(\xi, \beta_0) = \left( \frac{\partial \phi_{cl} \Phi_l}{\partial \beta_i} \right) \hat{H}^\text{BO} \left( \frac{\partial \phi_{cl} \Phi_l}{\partial \beta_j} \right)_{\beta = \beta_0} = \left( \frac{\partial}{\partial \beta_i} \frac{\partial}{\partial \beta_j} \langle \phi_{cl} \Phi_l | \hat{H}^\text{BO} | \phi_{cl} \Phi_l \rangle_{\phi_{cl}, l} \right)_{\beta = \beta_0}, \quad (13)
\]

\[
\mathcal{U}_l^\text{BO}(\xi, \beta_0) = \left( \phi_{cl} \Phi_l | \hat{H}^\text{BO} | \phi_{cl} \Phi_l \rangle_{\phi_{cl}, l} \right)_{\beta = \beta_0}, \quad (14)
\]

\[
\Delta \beta = \beta - \beta_0, \quad (15)
\]

where in Eqs. (12) and (13) we used the Hellmann–Feynman theorem as \( \phi_{cl} \Phi_l \) is an eigenfunction of \( \hat{H}^\text{BO} \). Note that the inclusion of vibrational an-
harmonic effects could be accomplished by higher order expansions in Eq. (12). However, separating nuclear dof into classical and quantum ones, should improve the quality of the harmonic approximation for the quantum nuclear dof since, typically, the anharmonic behavior is associated to the classical-like nuclear coordinates. Hence, in this Letter we disregard such quantum anharmonic effects. Eq. (12) means that for each \( \xi \) position where the wave function factorization is possible, \( \phi_{\nu,j}(\beta) \) can be obtained as a vibrational eigenfunction of a harmonic-like nuclear Hamiltonian operator, and hence the overall Hamiltonian eigenvalues are given by a specific combination of a BO eigenvalue with a vibrational one. Moreover, defining with \( r_n \) and \( p_n \) the cartesian nuclear coordinates and conjugated momenta we can express the nuclear kinetic energy operator as

\[
\hat{K} = \frac{1}{2} \mathbf{M}_{rr}^{-1} \mathbf{p}_{n}^2,
\]

(16)

where \( \mathbf{M}_{rr}^{-1} \) is the inverse of the usual diagonal mass tensor. From the definition of the conjugated momenta operators we can easily obtain the momenta operator transformation \( (\mathbf{p}_{n} \rightarrow \mathbf{\pi}_{n}) \) due to a coordinates transformation \( (r_n \rightarrow \eta_n) \),

\[
\mathbf{\pi}_{n} = ih \sum_{j} \left( \frac{\partial r_{n,j}}{\partial \eta_{n,j}} \right) \frac{\partial}{\partial r_{n,j}},
\]

(18)

or in vector notation

\[
\mathbf{\pi}_{n} = \mathbf{T}^{\dagger} \mathbf{p}_{n},
\]

(19)

\[
T_{j,j'} = \left( \frac{\partial r_{n,j}}{\partial \eta_{n,j'}} \right).
\]

(20)

Hence, the kinetic energy operator becomes

\[
\hat{K} = \mathbf{\pi}_{n} \cdot \frac{1}{2} \mathbf{M}_{rr}^{-1} \mathbf{\pi}_{n},
\]

(21)

\[
\mathbf{M}_{rr}^{-1} = \mathbf{T}^{-1} \mathbf{M}_{rr}^{-1} \mathbf{T}^{-\dagger},
\]

(22)

which is completely equivalent to the classical expression. From theoretical classical mechanics we know [4,5] that for each position of a subset of coordinates describing a hypersurface in configurational space, it is always possible to choose the complementary coordinates in such a way on the hypersurface the mass tensor, and hence its inverse, is a block diagonal matrix. If we then choose the nuclear degrees of freedom \( \eta_\nu = (\xi, \beta) \) in order to obtain a block diagonal mass tensor on the hypersurface defined by \( \beta = \beta_0 \), i.e., when the quantum coordinates are at their equilibrium positions \( \beta_0 \), and considering that \( \beta \) are ‘classically’ virtually fixed we have

\[
\begin{pmatrix}
\mathbf{M}_{\xi,\beta}^{-1} \\
\end{pmatrix}
= \begin{pmatrix}
\hat{D}_{\xi,\xi} & \hat{D}_{\xi,\beta} \\
\hat{D}_{\beta,\xi} & \hat{D}_{\beta,\beta}
\end{pmatrix}
\approx \begin{pmatrix}
\mathbf{D}_{\xi,\xi} & \mathbf{0} \\
\mathbf{0} & \mathbf{D}_{\beta,\beta}
\end{pmatrix}
\]

(23)

implying

\[
\mathbf{K} \approx \mathbf{K}_{\xi} + \mathbf{K}_{\beta},
\]

(24)

\[
\begin{pmatrix}
2\mathbf{K}_{\xi} \\
2\mathbf{K}_{\beta}
\end{pmatrix}
= \begin{pmatrix}
\mathbf{\pi}_{\xi}^\dagger \hat{D}_{\xi,\xi} \mathbf{\pi}_{\xi} \\
\mathbf{\pi}_{\beta}^\dagger \hat{D}_{\beta,\beta} \mathbf{\pi}_{\beta}
\end{pmatrix}
\]

(25)

(26)

where both \( \hat{D}_{\xi,\xi} \) and \( \hat{D}_{\beta,\beta} \) are evaluated at \( \xi, \beta_0 \). Finally, using these last equations into Eq. (12) we readily obtain, for the \( l' \) vibrational state on the \( l \)th BO surface

\[
\hat{H}_{e,l} \phi_{e,l,l'} = \mathcal{U}_{e,l,l'} \phi_{e,l,l'},
\]

(27)

\[
\begin{pmatrix}
\mathbf{K}_{\xi} \\
\mathbf{K}_{\beta}
\end{pmatrix}
= \begin{pmatrix}
\frac{\mathbf{A}}{2} & \mathbf{0} \\
\mathbf{0} & \mathbf{A}
\end{pmatrix}
\]

(28)

\[
\begin{pmatrix}
\mathcal{U}_{l,l'} \\
\mathcal{U}_{l,l'}^0
\end{pmatrix}
= \begin{pmatrix}
\mathcal{U}_{l,l'} - \mathcal{U}_{l,l'}^0 & \mathcal{K}_{\xi} \\
\mathcal{K}_{\xi} & \mathcal{K}_{\beta}
\end{pmatrix}
\]

(29)

where now in the notation of the overall Hamiltonian eigenvalue \( \mathcal{U}_{l,l'} \) we explicitly show its double index \( l, l' \) due to the combination of the \( l \)th BO surface with the \( l' \)th corresponding harmonic vibrational state. The last equations clearly show that the overall perturbed Hamiltonian eigenvalues given by

\[
\begin{pmatrix}
\mathcal{U}_{l,l'}(\xi) \\
\mathcal{U}_{l,l'}^0(\xi)
\end{pmatrix}
= \begin{pmatrix}
\mathcal{U}_{l,l'}(\xi, \beta_0) + \mathcal{K}_{\xi}(\xi, \beta_0, \pi_\xi) \\
\mathcal{K}_{\xi}(\xi, \beta_0, \pi_\xi)
\end{pmatrix}
\]

(30)

can be obtained using PMM to calculate the perturbed BO energy surfaces and via the corresponding Hessian matrices at each energy minimum, also
the ‘local’ quantum harmonic terms. Hence for each fixed classical position $\xi$ on every BO surface we have a set of quantum harmonic vibrational states defined by the local quantum harmonic well at $\xi, \beta_0$. The derivation described can be easily generalized for a multimolecular system, at least in the case the overall eigenfunction can be well approximated by the product of molecular wavefunctions.

4. The molecular polarizability

The results obtained in the previous two sections can be used to evaluate molecular polarizability for a given electronic state. This can be accomplished by first evaluating, via the electronic eigenfunction, the polarizability at $\xi, \beta_0$ on a given BO surface, and then averaging, with the correct statistical mechanical distribution, over the classical coordinates and conjugated momenta $\xi, \pi$. Note that the use also of the nuclear quantum harmonic wave functions in the calculation of the electric moment of a given Hamiltonian eigenstate, provides the same value since $\langle \phi_{i,j,f} | \beta | \phi_{i,j,f} \rangle = \beta_0$, i.e., for a given classical position $\xi$ the electric moment is fully defined by the BO electronic eigenfunction. Hence, using the equations of Section 2 we can evaluate, for a given homogeneous perturbing field, the energy on the $l$th BO surface and from this to identify for each $\xi$ position the corresponding $\beta_0$ (which is a function of the applied field). We can then obtain the polarizability into two ways. We can directly use the Hamiltonian perturbed eigenvectors $c$, obtained diagonalizing the BO perturbed Hamiltonian matrix evaluated at $\xi, \beta_0$, on the $x, y, z$ dipole matrices expressed in the unperturbed Hamiltonian eigenvectors basis set, also obtained at $\xi, \beta_0$:

$$\mu_{l,k} = c^T_l \Lambda_k c_l, \quad \Lambda_{ij} = \langle \phi^0_i | \mu_k | \phi^0_j \rangle, \quad k = x, y, z,$$

(31) (32) (33)

where $\phi^0$ are clearly the unperturbed BO Hamiltonian eigenfunctions evaluated as $\mu_l$ at $\xi, \beta_0$. In this way, updating the $\beta_0$ position, as the field is varied, the electric moment values for each $l$th electronic eigenstate can be collected as a function of the perturbing field, and hence the polarizability at fixed $\xi$ is obtained. Such a direct procedure can be replaced by the use of the perturbed BO energy, due to a homogeneous field aligned along one axis, to obtain molecular polarizability. In this case the perturbed BO energy at $\xi, \beta_0$, that we obtained by PMM, can be also expressed in terms of the corresponding unperturbed BO energy $\mathcal{U}_l^{BO}$, the perturbing field $E_k$ and intramolecular energy shift $\Delta \mathcal{U}_l^{\text{intra}}$,

$$\mathcal{U}_l^{BO}(\xi, \beta_0) = \mathcal{U}_l^{BO}(\xi, \beta_0) - \mu_{l,k}(\xi, \beta_0, E_k)E_k + \Delta \mathcal{U}_l^{\text{intra}}(\xi, \beta_0), \quad (34)$$

and so expanding up to the first order the perturbed electric moment in the field

$$\mu_{l,k}(\xi, \beta_0) \approx \mu_{l,k}^0(\xi, \beta_0) + \zeta_{l,k,k}(\xi, \beta_0)E_k \quad (35)$$

we obtain

$$\mathcal{U}_l^{BO} \approx \mathcal{U}_l^{BO} - \mu_{l,k}^0E_k - \zeta_{l,k,k}^0 E_k^2 + \Delta \mathcal{U}_l^{\text{intra}}, \quad (36)$$

where $\mu_{l,k}^0$ is the $k$ component of the unperturbed electric moment for the $l$th BO surface, evaluated at $\xi, \beta_0$, and $\zeta_{l,k,k}^0$ the unperturbed, i.e., evaluated at zero field, corresponding polarizability $k, k$ element. From second order quantum perturbation theory, we know that $\Delta \mathcal{U}_l^{\text{intra}}$ is given by minus one half of the perturbation interaction energy due to the change of electronic density $[6,7]$. Hence, from Eq. 36 we obtain

$$\Delta \mathcal{U}_l^{\text{intra}} \approx -\frac{1}{2} ( - \zeta_{l,k,k}^0 E_k^2 ) = \zeta_{l,k,k}^0 \frac{E_k^2}{2}, \quad (37)$$

and so

$$\mathcal{U}_l^{BO} \approx \mathcal{U}_l^{BO} - \mu_{l,k}^0E_k - \zeta_{l,k,k}^0 \frac{E_k^2}{2}. \quad (38)$$

We can proceed further expanding, at fixed $\xi, \mu_{l,k}^0$ and $\zeta_{l,k,k}^0$ in $E_k$ via $\beta_0(E_k)$:

$$\zeta_{l,k,k}^0(\xi, E_k) \approx \zeta_{l,k,k}^0(\xi, \beta_0^0) = \zeta_{l,k,k}^{0,0}, \quad (39)$$

$$\mu_{l,k}^0(\xi, E_k) \approx \mu_{l,k}^0(\xi, \beta_0^0) + \Delta \mu_{l,k}^0 E_k \frac{E_k}{2}, \quad (40)$$

$$\mu_{l,k}^{0,0} = \mu_{l,k}^0(\xi, \beta_0^0), \quad (41)$$

Note that the use also of the nuclear quantum harmonic terms $H_{\text{nuc}}$. Hence for each fixed classical position $\xi$ on every BO surface we have a set of quantum harmonic vibrational states defined by the local quantum harmonic well at $\xi, \beta_0$. The derivation described can be easily generalized for a multimolecular system, at least in the case the overall eigenfunction can be well approximated by the product of molecular wavefunctions.
\[ \Delta \alpha^0 = 2 \sum_j \left( \frac{\partial \mu^0_{i,k}}{\partial \beta^0_{0,j}} \right)_{\beta^0 = \beta^0_0} \left( \frac{\partial \beta^0_{0,j}}{\partial E_k} \right)_{E_k = 0} \]  

where \( \beta^0_0 \) is the position of the energy minimum at fixed \( \xi \) when no electric field is applied. Hence, Eq. (38) transforms into

\[ \mathcal{U}^{BO}_{i}(\xi, E_k) \simeq \mathcal{U}^{BO}_{i}(\xi, \beta^0_0(E_k)) - \mu^0_{i,k} E_k - \alpha_{i,k,k} \frac{E_k^2}{2}, \]  

(43)

\[ \alpha_{i,k,k} = \Delta \alpha^0 + \alpha^0_{i,k,k}. \]  

(44)

Eq. (43) clearly shows that plotting the \( \ell \)th BO energy shift \( \mathcal{U}^{BO}_{i} - \mathcal{U}^{BO}_{i,0} \) as a function of the field at fixed \( \xi \), we can easily obtain by quadratic fitting the complete polarizability \( \alpha_{i,k,k} \).

5. Application and conclusions

As a test system to illustrate the method described, we used a single water molecule interacting with a homogeneous electric field. In order to apply PMM for obtaining perturbed Hamiltonian eigenvalues on the BO hypersurfaces, we used the first 20 unperturbed eigenstates from CISD [8]/TVZ+(p,d) [9,10] calculations using a full valence SA-MCSCF [11]/TZV+(p,d) optimized molecular orbitals, all performed with GAMESS US package [12]. In Table 1 we compared the unperturbed energies from the above calculations with corresponding data as found in the literature [13–17]. In the previous Letter we showed that PMM can reproduce accurately the perturbed BO energies. In this Letter we evaluate a more sophisticated property such as polarizability, which can have a relevant dependence on molecular geometry. In Table 2 we compared the average polarizability, for ground and first excited (\( \tilde{\alpha} \)) states: PMM, using both dipoles and energies, CISD, variation perturbation (VP), RHF, SCF and CAS, and experimental values.

<table>
<thead>
<tr>
<th>Method</th>
<th>( \alpha )</th>
<th>( \tilde{\alpha} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMM (dipole)</td>
<td>4.47</td>
<td>44.12</td>
</tr>
<tr>
<td>PMM (energy)</td>
<td>4.70</td>
<td>47.16</td>
</tr>
<tr>
<td>CISD</td>
<td>6.90</td>
<td>49.74</td>
</tr>
<tr>
<td>VP/6-21G( ^a )</td>
<td>4.04</td>
<td>–</td>
</tr>
<tr>
<td>VP/6-31G( ^a )</td>
<td>4.41</td>
<td>–</td>
</tr>
<tr>
<td>VP/6-311G**( ^a )</td>
<td>5.42</td>
<td>–</td>
</tr>
<tr>
<td>RHF/TZP( ^b )</td>
<td>5.56</td>
<td>–</td>
</tr>
<tr>
<td>SCF/ANO2( ^c )</td>
<td>8.47</td>
<td>100.03</td>
</tr>
<tr>
<td>CAS/ANO2( ^c )</td>
<td>9.25</td>
<td>110.64</td>
</tr>
<tr>
<td>Experimental( ^d )</td>
<td>9.45</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) Ref. [18].
\( ^b \) Ref. [19].
\( ^c \) Ref. [13].
\( ^d \) Ref. [16].

Table 1
Vertical excitation energies (eV) for the low-lying singlet states of water

<table>
<thead>
<tr>
<th>State</th>
<th>Present work</th>
<th>CAS( ^a )</th>
<th>LR( ^b )</th>
<th>MRDCI( ^b )</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1 )( ^1 )B( _1 )</td>
<td>7.29</td>
<td>7.88</td>
<td>7.93</td>
<td>7.76</td>
<td>7.44( ^c )</td>
</tr>
<tr>
<td>( ^1 )A( _2 )</td>
<td>9.04</td>
<td>9.68</td>
<td>8.74</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( ^2 )A( _1 )</td>
<td>9.95</td>
<td>10.28</td>
<td>10.25</td>
<td>10.30</td>
<td>9.85( ^d )</td>
</tr>
<tr>
<td>( ^2 )B( _1 )</td>
<td>11.74</td>
<td>11.12</td>
<td>10.60</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( ^1 )B( _2 )</td>
<td>14.48</td>
<td>12.08</td>
<td>11.56</td>
<td>11.04( ^c )</td>
<td>–</td>
</tr>
</tbody>
</table>

\( ^a \) Calculated data from [13].
\( ^b \) Calculated data from [14].
\( ^c \) Experimental value from [15].
\( ^d \) Experimental value from [16].
\( ^e \) Experimental value from [17].
similar to the PMM ones). From the table it is also evident that only very sophisticated calculations (SCF, CAS) provide a molecular polarizability close to the experimental one, while the other ab initio calculations provide underestimated polarizabilities. PMM polarizabilities are underestimated as well and this is not due to a lack of convergence in the PMM calculations since polarizabilities are well converged using the first 10–15 unperturbed eigenstates (data not shown). Such a result probably reflects the fact that the unperturbed transition dipoles, obtained by CISD level of theory with the used atomic basis set, provide rather accurate perturbed energies [1] (a scalar property) but not very accurate perturbed dipoles (a vector property) or second order energy derivatives. This implies that in order to obtain the latter properties very accurately we must use more efficient procedures to estimate the unperturbed transition dipoles (e.g., CAS calculations with large extended ANO2). However, the present good performances of PMM in evaluating perturbed properties such as energy and electric moment, at relatively low computational costs, and the possibility to improve its accuracy using more reliable unperturbed transition dipoles, makes this method very promising for treating complex systems and in particular mixed quantum/classical systems.

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References