Stark resonance parameters for the $3a_1$ orbital of the water molecule

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Received 27 June 2017, revised 20 September 2017
Accepted for publication 4 October 2017
Published 30 October 2017

Abstract

The Stark resonance parameters for the $3a_1$ molecular orbital of H$_2$O are computed by solving a system of partial differential equations in spherical polar coordinates. The starting point of the calculation is the non-spherical quantum potential derived for this orbital from a single-center expanded Hartree–Fock orbital. The resonance positions and widths are obtained after applying an exterior complex scaling technique to describe the ionization regime for external fields applied along the two distinct $\hat{z}$ directions associated with the symmetry axis. Comparison is made with previous results for the $1b_1$ and $1b_2$ orbitals obtained from a spherical potential approximation.

Keywords: water molecule, Stark effect, resonance parameters

((Some figures may appear in colour only in the online journal)

1. Introduction

Despite the complexity that the multi-center nature of the water molecule entails, it has been the topic of numerous studies including laser-induced ionization and high-harmonic generation [1, 2], as well as electron capture and ionization processes in ion–molecule collisions [3–10]. Most calculations are within the framework of the independent electron model and use a multi-center description of the potential [10, 11]. A strong motivation to continue exploring this subject comes from the fundamental role which ionization plays in radiation damage of biological tissue.

In a previous study of the H$_2$O valence orbitals exposed to strong dc fields, we used an approach to determine the resonance parameters for a given geometry of the orbitals without multi-center integrals [12]. Based on the implementation of an exterior complex scaling method, a system of partial differential equations was solved numerically. The molecular potential was expressed as a spherically symmetric effective potential obtained from a single-center basis Hartree–Fock (HF) calculation [13]. The ionization parameters for the $1b_1$ and $1b_2$ molecular orbitals were explored over a range of electric field strengths.

Here we extend the approach to study the dc Stark problem for the $3a_1$ molecular orbital of H$_2$O. Given the orientation of this orbital with respect to the plane in which the two protons are located it is deemed necessary to go beyond the spherical effective potential approximation which was used for the $1b_1$ and $1b_2$ orbitals. This is accomplished by deriving a potential $V_{\text{eff}}(r, \theta)$ for the $3a_1$ orbital from the single-electron Schrödinger equation with HF orbital wavefunction and energy supplied as known quantities.

This paper is organized as follows: in section 2 the construction of the effective potential $V_{\text{eff}}(r, \theta)$ is presented. The required asymptotic corrections applied to the electronic potential are given in section 2.1, followed by a description of the problem in terms of a system of partial differential equations in section 2.2. Numerical results for the resonance parameters are presented in section 3, followed by conclusions in section 4. Atomic units ($\hbar = m_e = e = 4\pi\varepsilon_0 = 1$) are used throughout.

2. Non-spherical effective potential derived from molecular orbitals

The starting point for this work is the HF calculation of the H$_2$O molecule in a single-center Slater orbital basis [13]. Previously, we used the dominant parts of the $1b_1$ and $1b_2$ orbitals, namely the $np_z$ and $np_x$ parts, to derive spherically symmetric effective orbital-dependent potentials and applied
a Latter correction to guarantee the proper asymptotic behavior for the respective potential [12, 14].

Applying the same procedure to the $3a_1$ orbital, i.e., retaining the $np_z$ parts of the MO only leads again to a spherically symmetric effective potential. Since we are interested in the response of the orbital when applying an electric dc field along the symmetry axis (i.e., the $z$-axis), there is an obvious deficiency: the two protons (located in the $y-z$ plane) introduce a strong asymmetry, which leads to significant admixtures of $p$-type Slater orbitals in the Moccia Slater-type orbitals (STOs) [13].

The proposed method to address this problem is to define a reduced single-center Moccia wavefunction,

$$\psi_{3a_1}(r, \theta) = \sum_{n,l} c_{nlm} \varphi_{nl}(r, \theta).$$  \hspace{1cm} (1)

Here the $\varphi_{nl}(r, \theta)$ are Slater orbitals with $m = 0$ for the magnetic quantum number, and we limited the expansion to STOs of $2s$ and $2p_z$ type. The parameters are given in table 1 and three $2p_z$ orbitals are mixed with three $2s$-type orbitals. This set of coefficients represents a reduced selection of the expansion parameters given by Moccia for the ground state of the water molecule [13] also shown in table 1.

The probability densities for the $3a_1$ orbital as obtained from the properly normalized reduced expansion (1) and from the Moccia self-consistent results are shown in figures 1(a) and (b) respectively. The protons (in red) lie in the $y-z$ plane. As figure 1(a) indicates, the contributions to the density of the $2s$-type states reproduce the proper dependence of the $3a_1$ probability density with the polar angle $\theta$, as the broader hump is located on the negative $z$-axis in the same way as in the complete Moccia representation shown in figure 1(b).

In order to illustrate the fraction of the full Moccia expansion that our reduced wavefunction (1) represents, the projections of the probability densities over the $x-y$ plane are shown as contours of constant density in figure 2, for the height where the protons are located. From the complete Moccia representation of the $3a_1$ MO (dashed lines), one observes that the location of the protons (shown as red circles) has an influence on the shape of the upper lobe in the probability density, i.e., it introduces dependence on the azimuthal angle $\phi$. In our simplified expansion, where only $l = 0$, 1 and $m = 0$ symmetrical parts were included (shown with solid lines), the probability density misses to represent the proper azimuthal dependence that follows from the $m \neq 0$ parts.

The non-spherical effective potential corresponding to the STO expansion (1), $V_{\text{eff}}(r, \theta)$, is obtained from the Schrödinger equation in spherical polar coordinates,

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(r, \theta)\right] \psi_{3a_1}(r, \theta) = E_{3a_1} \psi_{3a_1}(r, \theta).$$  \hspace{1cm} (2)

For given $E_{3a_1}$ and $\psi_{3a_1}(r, \theta)$ it is straightforward to solve (2) for $V_{\text{eff}}(r, \theta)$. In order to use this potential to define a Hamiltonian for the $3a_1$ orbital in an electric field an asymptotic Latter correction needs to be applied.

Other strategies for finding an effective potential could be pursued, such as using a density functional, inserting the Moccia wavefunction, and then performing an azimuthal angle average. Ultimately, one would like to extend density functional theory (DFT) from finding ground-state energies to obtaining resonance positions and widths. This might be feasible using a combination of time-dependent DFT and Floquet theory. The goal of the present work is more modest: we calculate the response of an isolated molecular orbital in a simple approximation. Recently the problem of small molecules in a dc field has revealed the effect of electron–electron interactions on Stark resonance parameters [15]. It will be interesting to observe such effects for the water molecule in future work.

2.1. Interpolation and Latter correction of the effective potential

The non-central effective potential, $V_{\text{eff}}(r, \theta)$, leads no longer to an orbital of $(l, m)$ symmetry, i.e., $2p_z$. This reflects the geometry of the problem as a consequence of the location of the protons. The use of this more general potential implies that the Latter criterion [14], which ensures the proper asymptotic behavior of the potential, is not as straightforward to implement as in the case of the spherical potential where the correction applies beyond a determined $r$ value [12]. Now the correction must be implemented in the $r-\theta$ plane, by defining a $\theta$-dependent boundary beyond which the potential obtained from (2) rises above $-1/r$ in the asymptotic region.

We fix the $\theta$ coordinate at two extreme positions, such as $\theta = 0$ and $\pi$, to find the corresponding $r$ values, $r_0$ and $r_e$, for which $V_{\text{eff}}(r, \theta) = -1/r$ is satisfied, and then interpolate between them by introducing a $\theta$-dependent function. We use the function

$$r_{\text{match}}(\theta) = \bar{r} - (r_e - \bar{r})\cos \theta,$$

where $\bar{r} = (r_0 + r_e)/2$. With this approach we redefine the effective potential to be the non-central potential derived from

| $(n, l, m)$ | $c_{nlm}$ | $\zeta_n$ |
|-----------|-----------|-----------|
| (1, 0, 0) | Excluded  | −0.00848  | 12.600 |
| (1, 0, 0) | Excluded  | 0.08241   | 7.450  |
| (2, 1, 0) | Included  | 0.79979   | 1.510  |
| (2, 1, 0) | Included  | 0.00483   | 2.440  |
| (2, 1, 0) | Included  | 0.24413   | 3.920  |
| (2, 0, 0) | Included  | −0.30752  | 2.200  |
| (2, 0, 0) | Included  | −0.04132  | 3.240  |
| (2, 0, 0) | Included  | 0.14954   | 1.280  |
| (3, 2, 0) | Excluded  | 0.05935   | 1.600  |
| (3, 2, 0) | Excluded  | 0.00396   | 2.400  |
| (3, 2, 2) | Excluded  | −0.09293  | 1.600  |
| (3, 2, 2) | Excluded  | 0.01706   | 2.400  |
| (4, 3, 0) | Excluded  | −0.01929  | 1.950  |
| (4, 3, 2) | Excluded  | −0.06593  | 1.950  |
the reduced Moccia wavefunction using equation (2) when $r < r_{\text{match}}(\theta)$, and $-1/r$ otherwise.

The weighted functions used to construct the Moccia orbitals [13] imply a potential difficulty in our problem. Since these functions are not exact solutions of the Schrödinger equation but were obtained from the variational principle by implementing a self-consistent calculation [16], there may be regions in the $(r, \theta)$ domain where $\psi_{3a_1}(r, \theta)$ vanishes, whereas its second derivative remains finite; this produces a nodal line in the electronic potential. Thus finding a potential for which our approximate wavefunction satisfies a Schrödinger equation represents an intricate problem.

It turns out that the nodal region is so narrow that when solving the Schrödinger equation the kinetic energy term dominates and it is possible to obtain a solution that remains close to that obtained by the HF method [13], regardless of the fact that there is a region where the effective potential might diverge.

The probability density exhibits two humps indicating the positions of the protons, which is consistent with figure 1, and the effects of the mixing with the $s$-state. One may argue that one of the reasons this nodal region in the potential does not have a negative impact on the results is due to the way the $3a_1$ orbital responds to the effective potential by avoiding this region, its probability density being distributed as shown in figure 3. We implement a numerical interpolation of $V_{\text{eff}}(r, \theta)$ in order to ensure it continues smoothly over this problematic region.

The interpolation is achieved by collecting data from the evaluation of the potential on two sections of the $(r, \theta)$ grid in the vicinity of the nodal line, where the potential evaluates to finite values. Then a numerical interpolation was carried out between those regions in order to obtain a continuous function, $V_{\text{imp}}^{\text{intp}}(r, \theta)$, on the two-dimensional grid. The Latter correction is applied to the interpolated potential and the
The effective potential is defined according to (3):

\[ V_{\text{eff}}(r, \theta) = \begin{cases} 
V_{\text{eff}}^{\text{imp}}(r, \theta) & \text{for } r < r_{\text{match}}(\theta) \\
-1/r & \text{for } r > r_{\text{match}}(\theta) 
\end{cases} \] (4)

Figure 3(a) shows the probability density for the 3a_1 MO as a contour plot in the \(r-\theta\) plane as obtained from the reduced Moccia expansion in STOs (1). Figure 3(b) shows the same for the solution of the Schrödinger equation (2) using the interpolated \(V_{\text{eff}}(r, \theta)\), given in equation (4), with the Latter correction [14] applied in the asymptotic \(r\)-region.

The effective potential (4) results in the probability density shown in figure 3(b) and yields an orbital energy of \(-0.5579\) a.u. for the 3a_1 MO, with a relative change of 0.32% in comparison with the self-consistent result of Moccia [13] of \(-0.5561\) a.u.

As figure 3(b) indicates, the implementation of the Latter correction to the orbital-dependent potential obtained from equation (2), introduces a slight re-adjustment of the density, with a somewhat higher probability density in the region \(0 < \theta < \pi/2\). The probabilities for finding the electron at \(\pi/2 < \theta < \pi\) is 66.2% before the Latter correction is applied (figure 3(a)) and becomes 63.5% for the case shown in figure 3(b).

2.2. Exterior complex scaling using a smooth transition region

For our aim of computing the resonance parameters that describe the tunneling process a modified exterior complex scaling to the radial coordinates was implemented. In contrast with the exterior complex scaling method [12, 17–20], which scales the coordinate into the complex plane beyond some determined radius in order to avoid reflections from the edges of the mesh, we implement a modified technique in which the \(r\)-coordinate is extended into the complex plane by the phase function \(\chi(r)\), with \(r\) replaced by \(r^* = r \exp[i\chi(r)]\). The phase function \(\chi(r)\) is chosen to be very small for \(r\) values smaller than the Latter radius \(\bar{r}\). It then turns on to reach an asymptotic value \(\chi_s\) to provide exterior complex scaling without a hard radius at which a derivative discontinuity would have to be applied [21]. The gradual increment of the scaling function is implemented by the same...
function as used in [12] as
\[
\chi(r) = \frac{\chi_s}{1 + \exp\left[-\frac{\chi_s}{\Delta r}(r - r_s)\right]},
\]
where the parameters \(r_s\) and \(\Delta r\) were chosen for the function \(\chi(r)\) to rise smoothly from nearly zero to \(\chi_s\) at \(r\)-values just outside where the Latter correction is applied, i.e., \(r_s > r_{\text{match}}\).

A non-Hermitian Hamiltonian is obtained as a result of considering the additional terms that the modified complex scaling to the radial coordinate introduces in the Schrödinger equation. The complex wavefunction is separated into real and imaginary parts, \(\psi_{R/I}(r, \theta)\), such that the problem of describing the ionization regime of the 3a_1 MO under an external dc field applied along the orientation axis of the orbital is expressed in terms of a system of partial differential equations for the real and imaginary parts of \(\psi(r, \theta)\) in spherical polar coordinates given explicitly as equation (9) in [12]. Schematically the equations are extensions of the field-free Schrödinger equation (2) and \(\psi(r, \theta)\) satisfies
\[
\left[-\frac{1}{2}
abla^2 + V_{\text{eff}}(r, \theta) \pm F_0 \hat{z}\right] \tilde{\psi} = (E_R - i\Gamma/2)\tilde{\psi},
\]
where \(E_R\) is the resonance position and \(\Gamma\) the width. Compared to equation (2) the Hamiltonian in equation (6) contains the interaction with the external field and complex scaling is responsible for the replacement \(E_{3a_1} \rightarrow E_R - i\Gamma/2\); while \(\tilde{\psi}\) remains square integrable.

The domains of \(r\) and \(\theta\) values were restricted to the intervals \(r \in [\epsilon, r_{\text{max}}]\) and \(\theta \in [\eta, \pi - \eta]\), with typical values \(\epsilon = 10^{-2}\) a.u, \(\eta = 10^{-2}\), \(r_{\text{max}} = 28\) a.u. In the limit of low field strengths, i.e., \(F_0 = 0.05, 0.06\), the value of \(r_{\text{max}}\) was increased to 40 a.u. in order to ensure the outer turning points lie inside the grid, as the tunneling barrier extends to larger \(r\).

The problem of finding a solution of the Schrödinger equation for the 3a_1 molecular orbital with contributions of 2s and 2p-type states requires a set of boundary conditions that describes the properties of the orbital on the grid. In contrast with the \(m = \pm 1\) solutions obtained for the 1b_1 and 1b_2 MOs of H_2O [12], Neumann boundary conditions were implemented for the angular coordinate \(\theta\) in order to obtain an eigenstate and orbital energy consistent with the variational results [13]. This choice of boundary conditions, that the derivative with respect to \(\theta\) vanishes at the limits of the mesh \((\theta = 0 \text{ and } \theta = \pi)\), leads to solutions \(\psi_{R/I}(r, \theta)\) with a probability density consistent with the \(3a_1\) orbital, as shown in figure 3. The physical parameters of interest, namely the resonance position, \(E_R\), and width, \(\Gamma = -2E_I\), that characterize the tunneling process of the quasi-stationary state when an external electric dc field is applied along the \(\pm \hat{z}\) directions, were found by solving the system of partial differential equations [12] for a set of field strength values, \(F_0\), as if it were an inhomogeneous problem. In the vicinity of a location in the \((r, \theta)\) plane where the probability amplitude is expected to be large, a two-parameter root search was implemented to determine \(\{E_R, E_I\}\), the complex energy that maximizes the probability density amplitude in the 2d-grid.

### 3. Stark resonance parameters

Results from applying the procedure described in section 2 are shown in figures 4 and 5.

The resonance positions \(E_R\) are shown in figure 4 for external fields applied along the \(\pm \hat{z}\) directions (red triangles/blue circles) for a range of external field strengths. For reference, the resonance positions obtained for the 1b_1 and 1b_2 MOs using a spherically symmetric potential, \(V_{\text{eff}}(r)\), are also indicated in the form of dashed and dotted-dashed lines respectively. For zero field strength \(F_0 = 0\) self-consistent eigenenergies obtained by Moccia [13] are included as black crosses for the three valence orbitals of interest. As expected, the resonance position for the \(3a_1\) orbital is bracketed by those for the 1b_1 and 1b_2 orbitals.

It can be noticed that for external fields applied along the \(-\hat{z}\) direction, where most of the density is located, the field...
strength \( F_0 \) has to be strong, i.e., \( F_0 > 0.1 \) a.u., for the resonance position to change appreciably. On the other hand, the resonance position for fields applied along \( \hat{z} \) appears to be more sensitive at weaker fields. However the barrier appears to be longer for external fields applied along the \( +\hat{z} \) direction, at a field strength of about \( F_0 = 0.2 \) a.u. the position values cross, indicating a higher sensitivity of the resonance positions for fields applied along the negative \( \hat{z} \) direction as the field strength is increased further.

Figure 5 shows the resonance widths corresponding to external fields applied along the \( \pm \hat{z} \) directions, as a function of the field strength \( F_0 \). The results obtained with a symmetric effective potential, \( V_{\text{eff}}(r) \), for the \( 1b_1 \) and \( 1b_2 \) MOs are also shown as dashed and dotted-dashed lines for comparison purposes.

In analogy to the \( m = \pm 1 \) orbitals, the ionization rates for the \( 3a_1 \) MO, associated with the lifetime of the decaying state via \( \Gamma_{\tau} = 1 \), exhibit a threshold behavior at the weaker field strengths. Interestingly, for the two directions of the applied field, we find a lower critical field strength for the \( 3a_1 \) orbital in comparison to what the more weakly bound orbital, \( 1b_1 \), indicates. In the tunneling region, the \( 3a_1 \) orbital for fields applied along the \( -\hat{z} \) direction (blue squares) shows an ionization rate that is about one order of magnitude larger than the ionization rate for fields applied in the opposite direction (red triangles), this gap becomes narrower as the field strength increases toward the over-barrier regime.

The results are summarized in table 2 for further reference, to allow comparison with future calculations. The resonance parameters for the \( 1b_1 \) and \( 1b_2 \) orbitals are also included as a reference.

4. Conclusion

The Moccia single-center HF solution for the \( 3a_1 \) orbital of \( \text{H}_2\text{O} \) has been investigated to understand its response to a strong external dc electric field. We generalized a method to obtain an effective potential to take into account \( s-p \) type Slater orbital mixing included in the Moccia orbital. We ignored small \( l > 2 \) and particularly \( m = 2 \) contributions to limit the form of the effective potential to \( V_{\text{eff}}(r, \theta) \).

This permitted to study the relationship of the resonance parameters (position and width) to the neighboring valence orbitals \( 1b_1 \) and \( 1b_2 \) which were treated in a simplified approach before \( V_{\text{eff}}(r) \) only, i.e., \( 1b_1 \approx 2p_z \) and \( 1b_2 \approx 2p_y \). Interestingly, the \( 3a_1 \) orbital is found to ionize more easily than \( 1b_1 \) or \( 1b_2 \) irrespective of the field direction along \( \hat{z} \). The work should serve as motivation for further studies of molecular orbitals of water using more sophisticated wave functions.

Acknowledgments

The financial support from NSERC of Canada is gratefully acknowledged.

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