



Effect of dipole moments on orientation and alignment of a bounded molecule



Sonia Lumb^a, Shalini Lumb^{b,*}, K.D. Sen^c, Vinod Prasad^d

^a Department of Physics and Electronics, Rajdhani College, University of Delhi, New Delhi, 110015, India

^b Department of Physics, Maitreyi College, University of Delhi, New Delhi, 110021, India

^c School of Chemistry, University of Hyderabad, Hyderabad, 500046, India

^d Department of Physics, Swami Shraddhanand College, University of Delhi, New Delhi, 110036, India

ARTICLE INFO

Article history:

Received 30 November 2016

Received in revised form

10 February 2017

Accepted 13 February 2017

Available online 20 February 2017

Keywords:

Bounded diatomic molecule

Deng-Fan oscillator potential

Orientation

Alignment

ABSTRACT

A diatomic molecule modeled by Shifted Deng-Fan (SDF) oscillator potential and restricted to a small region of space has been considered. Energy spectra and radial matrix elements have been calculated using an accurate nine-point finite difference method. Orientation and alignment is generally studied by taking into account only the permanent dipole moment of the molecule. However, in this work, dependence of these properties on the actual set of matrix elements has been explored. A comparative study of the two has been presented. Effect of boundary radius and applied field strength has also been studied.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Molecular orientation and alignment play a fundamental role in the interaction of a molecule with other molecules, atoms or electromagnetic fields. The subject of orienting and aligning a molecule by various techniques has held a center stage in the field of research on molecular physics for many years [1]. The prime motivation for this study lies in its significant role in chemical reaction dynamics which aims to understand the chemistry in detail by probing chemical reactions on the scale of single reactive collisions between molecules. It is possible to control the quantum states and the geometrical orientation of the colliding molecules and also to measure these properties of reaction products and hence understand their effect on reactions under study.

A sufficiently intense laser pulse is capable of aligning the molecular axis along the polarization vector of laser. Molecular alignment can be achieved by manipulating the interaction between permanent or induced dipole moment of molecules and external fields. There is theoretical and experimental evidence that moderately intense lasers are capable of inducing sharp and controllable alignment [2]. The degree of alignment depends upon

the intensity of the applied laser field. But the intensity of the field has to be low enough to prevent ionisation or dissociation of the molecules. The degree of alignment also decreases with an increase in temperature. Laser-induced molecular alignment plays a major role in molecular processes like field ionization [3] and the generation of high-order harmonics [4].

Molecular spectra can be classified as arising due to a combination of electronic, vibrational and rotational transitions. However, if the considered temperatures are low enough so that the molecule is in the ground electronic and vibrational states, it is just the transitions between the rotational levels that decide the behaviour of the molecule. The vibrational and electronic transitions are thus frozen.

Many potential models such as Morse potential [5–7], Wood-Saxon potential [8], Deng-Fan (DF) oscillator potential [9] etc. have been used in the literature to describe a diatomic molecule. The trigonometric Pöschl-Teller potential used to describe the diatomic molecular vibration has been used by Hamzavi and Ikhdair to obtain approximate bound state solutions of the Schrödinger equation for an arbitrary l -state [10]. Rajabi and Hamzavi [11] analytically solved the Schrödinger equation for the Coulomb potential with a novel angle-dependent part using Nikiforov-Uvarov method. Further, molecular models under external constant magnetic and Aharonov-Bohm flux fields have

* Corresponding author.

E-mail address: shalini_lumb@hotmail.com (S. Lumb).

been extensively studied by Ikhdaïr et al. [12]. As shown by Hamzavi et al., the Tietz-Hua potential is one of the model potentials which depicts vibrational motion of the molecules quite accurately for moderate and higher ro-vibrational quantum numbers ([13] and references therein). DF potential qualitatively represents the Morse potential and shows the correct asymptotic behavior as internuclear distance tends toward zero and infinity [14]. Hence, we use the DF potential shifted by the dissociation energy (shifted DF potential (SDF) [15]) to model a diatomic molecule. The potential is modified due to the imposed boundary condition which causes the wavefunctions to vanish at a radial distance r_0 .

Bounded molecules can be found in nature in form of Zeolites and fullerene cages. They are also present as impurities in quantum dots and other semiconductor heterostructures. Such impurities have great influence on the functioning of nano devices. An enormous amount of work has been carried out in literature in order to study the influence of boundary on the properties of atoms and molecules [16]. It has been found to modify various system properties such as refractive index, polarizability and susceptibility etc. [17,18]. Therefore, it is pertinent to explore the effect of boundary on the orientation and alignment of a molecule as well.

Orientation of molecules strongly depends on the radial matrix elements. In case of a free molecule it is a good approximation that radial matrix elements do not change with change of rotational levels in a given vibrational state. Hence, interaction of the applied electric field E_s with the molecule is taken as $-\mu_0 E_s \cos \theta$ where μ_0 is permanent dipole moment of the molecule, and θ is the angle between the molecular axis and the electric field direction. As can be seen in Section 4, the radial matrix elements show quite a dependence on boundary radius r_0 . Therefore, we have performed our calculations for two sets of radial matrix elements (a) only '0000' where '0000' represents the transition $\langle 00|r|00 \rangle$, i.e., $v=0, J=0 \rightarrow v=0, J=0$ which corresponds to permanent radial matrix element. In this case, calculations have been performed using this matrix element for all the transitions. (b) all matrix elements, i.e., $\langle 0J|r|0J' \rangle$, where J and J' range from 0 to 25. In this case, actual values of the transition matrix elements calculated numerically for all transitions have been used. The aim of the present work is to study the effect of using the actual matrix elements on the properties like orientation and alignment. We thus show that in case of bounded molecules, one needs to take into account actual values of all radial matrix elements for a better understanding of behaviour of molecules in external fields.

The paper is organized as follows. Section 2 deals with the theoretical model followed by results and discussion in Section 3. Finally, conclusion of work done is presented in Section 4.

2. Theory and computational details

A diatomic molecule modelled by SDF potential is studied. It is considered to be bounded by an infinite potential wall at a radial distance r_0 from it. The SDF potential is defined as (atomic units are used throughout, i. e., $(\hbar = m_e = e = 1)$)

$$V(r) = D_e \left[\frac{b^2}{(e^{ar} - 1)^2} - \frac{2b}{e^{ar} - 1} \right], b = e^{ar_e} - 1, r \in (0, \infty). \quad (1)$$

The parameters D_e , r_e , a and r denote the dissociation energy, equilibrium internuclear distance, the range of the potential well and internuclear distance, respectively. The complete wave functions are written as a product of radial, $U_{nl}(r)/r$, and angular, Y_{lm} , parts as follows

$$\psi_{nlm}(\mathbf{r}) = \frac{U_{nl}(r)}{r} Y_{lm}(\theta, \phi). \quad (2)$$

Table 1

Some of the energy levels for $D_e = 15.0$ a.u., $a = 0.10$ a.u., $r_e = 0.8$ a.u. for DF potential. The data is in atomic units. The present results are for $r_0 = 50$ a.u. while those available in literature are for unbound molecules.

State	Present result	Ref. [20]	State	Present result	Ref. [14]
2p	4.219178	4.219180	7s	13.393325	13.393327
3p	7.724761	7.724764	7p	12.978281	12.978283
3d	5.845767	5.845770	7d	12.587910	12.587911
4p	9.883518	9.883524	8s	13.801171	13.801172
4d	8.707104	8.707111	8p	13.490995	13.490997
4f	7.586412	7.586418	8d	13.203413	13.203414

Using the above ansatz and employing the separation of variables technique Schrödinger equation can be separated into radial and angular parts and solved for the wavefunctions and eigen energy levels. The radial Schrödinger equation is given by

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) + V_b(r) \right] U_{nl}(r) = E_{nl} U_{nl}(r) \quad (3)$$

where $V(r)$ is the SDF potential defined in Eq. (1) and $V_b(r)$ is the boundary potential defined as

$$V_b(r) = \begin{cases} 0 & ; r < r_0 \\ \infty & ; r \geq r_0. \end{cases} \quad (4)$$

n and l denote the radial and orbital angular momentum quantum numbers and E_{nl} are the energy eigenvalues or the rovibrational energy states of the molecule, the usual notation for which is (v, J) where v and J represent the vibrational and rotational quantum numbers respectively. Equation (3) is solved for the ground vibrational state using nine point finite difference approach. The obtained rotational states are discrete having both positive and negative energies. Positive states correspond to the rotational dissociation of the molecule. The solution of the Schrödinger equation allows us to calculate the radial as well as the complete matrix elements of the form $\langle \psi_i | r^n | \psi_j \rangle$ and $\langle \psi_i | r^n \cos^n(\theta) | \psi_j \rangle$, $n = 1, 2$ respectively. We fix a as 0.10 a.u., r_e as 0.8 a.u. and D_e as 0.5 a.u. along with various values of r_0 to study the orientation and alignment variations.

The molecule is subjected to a radiation with electric field strength $E_s = E_0 \cos(\omega t)$ polarized along the z direction. For a permanent dipole moment μ along the internuclear axis and polarizability components α_{\parallel} and α_{\perp} parallel and perpendicular to the axis, the interaction potentials are defined as [19].

$$V_{\mu}(\theta) = -\mu E_s \cos \theta \quad (5)$$

and

$$V_{\alpha}(\theta) = -\frac{1}{2} E_s^2 (\alpha_{\parallel} \cos^2 \theta + \alpha_{\perp} \sin^2 \theta) \quad (6)$$

Equation (6) refers to the interaction of the field with the induced dipole moments. The Schrödinger equation in the presence

Table 2

Some of the energy levels for $D_e = 0.5$ a.u. and boundary radius, $r_0 = 5.0$ and 50 a.u. for SDF potential. The data is in atomic units.

State (vj)	$r_0 = 5$	$r_0 = 50$	State (vj)	$r_0 = 5$	$r_0 = 50$
0 0	-0.075175	-0.133158	0 10	4.364466	0.043515
0 1	0.171873	-0.038605	0 15	8.290253	0.083026
0 2	0.458732	-0.004990	0 20	13.330766	0.133553
0 3	0.786198	0.004891	0 25	19.469539	0.195013

Download English Version:

<https://daneshyari.com/en/article/5160389>

Download Persian Version:

<https://daneshyari.com/article/5160389>

[Daneshyari.com](https://daneshyari.com)