



# Entanglement for Qubit and Qudit in Single Photoionization of Rotationally State Selected, Oriented $C_{3v}$ Polyatomic Molecules

M Chakraborty<sup>a\*</sup> & S Sen<sup>b</sup>

<sup>a</sup>Department of Physics, Asansol Girls College, Asansol, West Bengal- 713 304 India

<sup>b</sup>Department of Physics, Triveni devi Bhalotia College, Raniganj, West Bengal- 713 347 India

Received 6 February 2022; accepted 25 April 2022

Multidimensional quantum systems (qudits), as a generalization of two-level quantum systems (qubits), can exhibit distinct quantum properties, provide higher capacity and noise robustness in quantum communications. Qudits also offer higher efficiency and flexibility in quantum computing. Present paper studies the bipartite entanglement between a molecular photoion (qudit) and photoelectron (qubit) produced in the photoionization from rotationally state selected, oriented polyatomic molecule without observing spin-orbit interaction (SOI). In absence of SOI, Russell-Saunders (RS) coupling is applicable. The dimension of ionic qudit depends on its electronic state. The degree of entanglement is quantified by the concurrence obtained from the elements of density matrix (EDM) for photoionization. The theoretical formulation for entanglement has been developed for photoionization of rotationally state selected, oriented  $C_{3v}$  molecules. It is applied, as an example, to photoionization in  $|3a_1^2$  orbital of a state selected oriented  $CH_3I$  in a pure  $|JK_J M_J\rangle$  rotational state. We find that the entanglement depends significantly on the rotational states of the molecule as well as either or both on the directions of molecular orientation, of spin quantization, and of the incident beam along with its polarization. A significant effect on entanglement properties due to the circular dichroism (CD) has also been observed.

**Keywords:** Quantum entanglement; Qudit; Qubit; photoionization; Concurrence; Density matrix; Circular dichroism

## 1 Introduction

Quantum entanglement<sup>1</sup> is the essential resource of quantum information theory (QIT)<sup>2,4</sup>. Recently, efforts have been given to characterize the entanglement properties for higher dimensional systems. In fact, entangled state of d-dimensional quantum systems ( $d > 2$ ), the qudits, can improve measurement resolution<sup>5,6</sup> and the use of qudit can reduce the number of qubits by a factor of  $\log_2 d$ <sup>7,8</sup>. Multipartite and qudit systems are also useful for developing quantum communication protocols which provides greater security in quantum cryptography<sup>9,10</sup> and reduces circuit complexity<sup>11,12</sup> compare to qubit system. Several groups<sup>8,13-15</sup> have already investigated entanglement of photonic qudits. Though photons are the fastest and excellent carrier of information and they may be entangled however they are not suitable for long term storage as well as not correlated<sup>16</sup>. Ions and electrons are stable, easily detectable and capable of storing information for a long period of time. Electrons are the lightest particle and can move with speeds comparable to photon. It has been already suggested that electron spin can be used for quantum computation<sup>1,11</sup>.

Photoionization is one of the simplest processes in atoms and molecules for producing bipartite entangled and correlated states of qubit (emitted photoelectron with spin  $\frac{1}{2}$ ) and qudit (residual photoion with spin  $\frac{3}{2}$  which is  $\geq 1$ ) with non-zero rest mass. Theories have been developed for studying entanglement of an ionic qudit and electronic qubit produced in single-photoionization<sup>17</sup> as well as in double-photoionization<sup>18,19</sup> for atoms. Several workers have investigated entanglement properties in single-step double photoionization (DPI)<sup>20</sup> and two-step DPI<sup>11,21,22</sup> for electronic qubits as well as for qudit-qubit<sup>23</sup> system in randomly oriented linear molecules. However, the studies of photoionization of state selected and oriented molecules have been known<sup>24,25</sup> to be potentially richer source of information on photoionization dynamics than those performed on randomly oriented molecules.

In this article we, probably the first time, study the entanglement properties of bipartite states of an electronic qubit (say  $e$ ) and ionic qudit (say  $M^+$ ), without observing SOI, produced by single-step

\*Corresponding author: (E-mail: bminakshi@yahoo.com)

photoionization from rotationally state selected and oriented polyatomic molecule following the absorption of a single photon. The entanglement is generated between the photoelectron and residual photoion due to the Coulombic forces inside the molecule. The dimension of the Hilbert space of the qudit depends upon the electronic state of the residual photoion  $M^+$ . We have investigated photoionization of those molecular systems prepared in a single rotational state of their ground electronic level by an electrostatic hexapole field<sup>25</sup> and can be oriented<sup>26</sup> in space by applying a weak homogeneous electric field  $E$  in their gas phase. The angle-resolved photoelectron spectroscopy (ARPES) caused by absorption of a single photon in molecules oriented in space in a pure rotational state of their ground electronic motion provides an opportunity to study simultaneously the effects of gaseous molecular orientation and of its nuclear rotation on the bipartite entanglement between an electronic qubit and ionic qudit. The theoretical formulations developed herein have been applied to symmetric top polar molecules  $CY_3X$  (where  $X$  is a halogen (F, Cl, Br, I) and  $Y$  is a H, F, or methyl), belonging to  $C_{3v}$  point group, have very successfully been state selected and orientated using electrostatic hexapole techniques<sup>25</sup>. We have also studied the effect of circular dichroism (CD) on the entanglement in this article. Circular dichroism in photoelectron angular distribution has added an extra dimension to study of photoionization processes in oriented molecules. Several theoretical studies have predicted a circular dichroism in the angular distribution (CDAD) of photoelectrons for oriented molecules<sup>27-29</sup> and also in rotationally state selected, oriented molecules<sup>24,30</sup>. Experimental studies of CDAD for oriented diatomics (CO, NO), benzene, and  $CH_3I$  ( $C_{3v}$  molecule) have been performed by Westphal *et al.*<sup>31</sup>.

Bell's theorem<sup>1</sup> provides us a necessary and sufficient condition for the existence of entanglement only for pure bipartite states of qubits. On the other hand, the negative partial transpose (NPT) condition, suggested by Peres<sup>32</sup> & Horodecki<sup>33-35</sup>, is a necessary and sufficient for entanglement of both pure and mixed qubit states. A fundamental fact is that this necessary and sufficient condition for entanglement is valid when the dimension of the Hilbert space of a system does not exceed six. Therefore in this article as a measure of free entanglement, we have used concurrence<sup>36,37</sup> which can be generalized to study

entanglement for higher dimensional cases and can also quantify the degree of entanglement. However to investigate bound entanglement Horodecki's inequality condition<sup>7,33</sup> have been applied.

In section 2, we develop the general expressions for density operator (DO) and EDM for ARPES in rotationally state selected and oriented molecules. The theory is used to study photoionization in rotationally state selected and oriented symmetric top  $C_{3v}$  molecule in section 3. A quantitative application of entangled properties in the photoionization from  $13a_1^2$  orbital of a state selected, oriented  $CH_3I$  molecule is given in section 4. Section 5 contains the conclusion part of this work.

## 2 Theoretical Formulation for Density operator and elements of density matrix for qudit-qubit system

One step single photoionization (SPI) process of a rotationally state selected and oriented molecule  $M$  due to absorption of a single photon of frequency  $\nu_r$ , can schematically be represented by

$$h\nu_r (|l_r| = 1, m_r) + M |i\rangle \rightarrow M^+ |f\rangle + e_p(\vec{k}; \mu, \hat{u}) \quad \dots (1)$$

Here  $M^+$  denotes the residual singly ionized molecule. The propagation vector of the emitting photoelectron  $e_p$  (of orbital angular momentum  $l$ , spin angular momentum  $s=1/2$  and mass  $m_p$ ) is  $\vec{k} = (k, \theta_k, \phi_k)$  such that its kinetic energy is given by  $\varepsilon = \hbar^2 k^2 / 2m_p$ .  $\mu (= \pm 1/2)$  represents the projection of the spin angular momentum of the electron, ejected in the  $(p\tau h l)$  channel<sup>24</sup> ( $p$  stands for irreducible harmonics (IR) of the point group of the molecule,  $\tau$  denotes a component of this IR if its dimensionality is greater than one, and  $h$  distinguishes between different bases of the same IR corresponding to the same value of  $l$ ), along its spin quantization direction  $\hat{u} = (\theta_u, \phi_u)$  (Fig. 1).

Here,  $E_r = h\nu_r$  and  $|l_r| = 1$  are respectively the energy and the angular momentum of the incident photon absorbed by the molecule  $M$ . The state of polarization of the photon is represented by the parameter  $m_r$ . Where  $|i\rangle$  and  $|f\rangle$  are the bound electronic states of  $M$  with energy  $E_i$  and the residual photoion  $M^+$  possessing energy  $E_f$  respectively. Let  $\omega \equiv (\alpha, \beta, \gamma)$  be the sets of Euler angles needed to

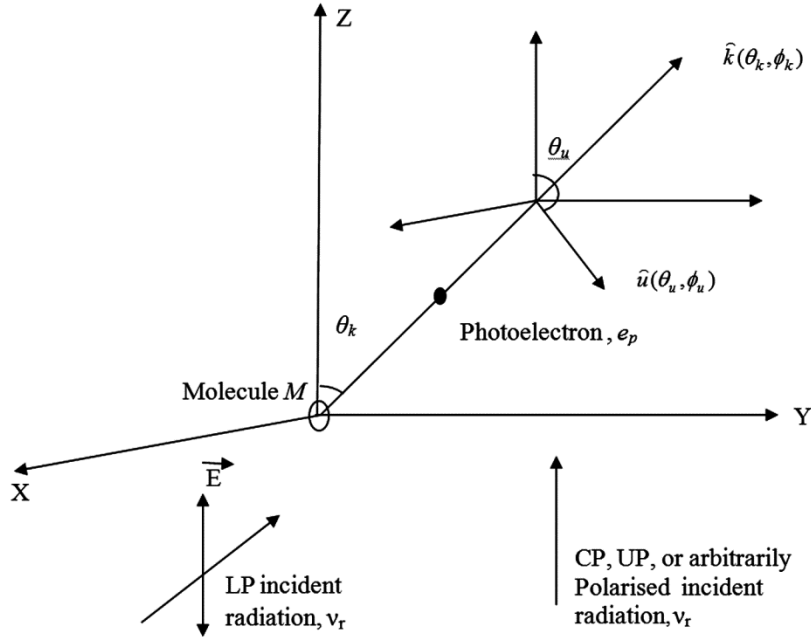


Fig. 1 — Emission of photoelectron ( $e_p$ ) from the molecule ( $M$ ) following photoabsorption.

specify the orientation of molecular frame of reference with respect to space frame of reference and  $\omega_p \equiv (\hat{p}(\theta_p, \phi_p), 0)$  are sets of Euler angles which rotates the space frame into photon frame. Here the ket  $|1m_r\rangle$  is used to designate a photon state in its own frame of reference. If  $|1\lambda_r\rangle$  is the photon state in the molecule-fixed frame, we can write<sup>38</sup>

$$|1m_r\rangle = \sum_{m_r} D_{m_r, \lambda_r}^1(\omega_p) |1\lambda_r\rangle. \quad \dots (2)$$

where  $D$ s are the well known rotational harmonics.

Here  $(\vec{L}_0, \vec{L}_f)$  are the orbital angular momenta and  $(\vec{S}_0, \vec{S}_f)$  are the spin angular momenta of  $M$  and  $M^+$  respectively. We use the symbols  $M_{L_0}, M_{S_0}, M_{L_f}$  and  $M_{S_f}$  to represent the respective projections of  $\vec{L}_0, \vec{S}_0, \vec{L}_f$  and  $\vec{S}_f$  along the polar axis of the space frame. The electronic states of  $M$  and  $M^+$  in L-S coupling are given by<sup>39</sup> as  $|i\rangle \equiv |L_0, S_0, M_{L_0}, M_{S_0}\rangle |JKM\rangle$  and  $|f\rangle \equiv |L_f, S_f, M_{L_f}, M_{S_f}\rangle$  respectively. We have then

$$\begin{aligned} \vec{L}_0 + \vec{L}_f &= \vec{L}_f + \vec{L} \\ \vec{S}_0 &= \vec{S}_f + s (= \frac{1}{2}) \end{aligned} \quad \dots (3)$$

The density operator for the process SPI (1) in the L-S coupling can be written as

$$\begin{aligned} \rho &= \frac{K}{(2L_0 + 1)(2S_0 + 1)} \\ &\times \sum_{M_{L_0}=-L_0}^{L_0} \sum_{M_{S_0}=-S_0}^{S_0} F_p(|i; 1m_r\rangle \langle i; 1m_r|) F_p^\dagger. \end{aligned} \quad \dots (4)$$

Here  $F_p = \left( \frac{4\pi m_p \alpha^3 E_r^3}{3\hbar^2 e^4} \right)^{1/2} \sum_{i=1}^n \hat{\xi}_{m_r} \hat{r}_i$  is the photoionization operator which represents the interaction of the atomic electrons (whose number is  $n$ ) with the incident photons in the  $E1$  dipole approximation and  $K = 3\pi \left( \frac{e^2}{\alpha E_r} \right)^2$  with  $\alpha$  the dimensionless fine structure constant<sup>40</sup>.  $\hat{\xi}_{m_r}$  is a spherical unit vector<sup>40</sup> which specifies polarization of electromagnetic wave incident in the process (1). The required EDM can be written as

$$\begin{aligned} \langle L_f S_f M_{S_f}; \mu \hat{u} \vec{k}_p | \rho^{SPI} | L_f S_f M_{S_f}'; \mu \hat{u} \vec{k}_p \rangle &= \\ \sum_{M_{L_f}=-L_f}^{L_f} \langle L_f S_f M_{L_f} M_{S_f}; \mu \hat{u} \vec{k}_p | \rho | L_f S_f M_{L_f} M_{S_f}'; \mu \hat{u} \vec{k}_p \rangle. \end{aligned} \quad \dots (5)$$

Here  $\langle L_f S_f M_{S_f}; \mu \hat{u} \vec{k}_p | F_p | L_0 S_0 M_{S_0}; 1 m_r \rangle$  is the photoionization amplitude. The normalized eigen functions for a  $|JK_J M_J\rangle$  rotational state<sup>41</sup> of the qudit-qubit system are

$$\langle \omega | JK_J M_J \rangle = \left( \frac{2J+1}{8\pi^2} \right)^{1/2} D_{K_J M_J}^J(\omega) \quad \dots (6)$$

Thus the probability that the polar axis of the molecule in its  $|JK_J M_J\rangle$  rotational state between  $\beta$  and  $\beta+d\beta$  becomes<sup>24</sup>

$$\begin{aligned} P_{JK_J M_J}(\beta) &= \int \langle JK_J M_J | \omega \rangle \langle \omega | JK_J M_J \rangle d\alpha d\beta \\ &= (-1)^{K_J - M_J} \frac{1}{2} (2J+1) \sum_{n=0}^{2J} (2n+1) \begin{pmatrix} J & J & n \\ K_J - K_J & 0 & 0 \end{pmatrix} \\ &\times \begin{pmatrix} J & J & n \\ M_J - M_J & 0 & 0 \end{pmatrix} P_n(\cos \beta). \end{aligned} \quad \dots (7a)$$

This expression for probability takes a particularly simple form<sup>24</sup>

$$P_{JK_J M_J}(\beta) = \frac{1}{2} \sum_{n=0}^{2J} (2n+1) \bar{P}_n P_n(\cos \beta), \quad \dots (7b)$$

where

$$\begin{aligned} \bar{P}_n &= (-1)^{K_J - M_J} (2J+1) \begin{pmatrix} J & J & n \\ K_J - K_J & 0 & 0 \end{pmatrix} \\ &\times \begin{pmatrix} J & J & n \\ M_J - M_J & 0 & 0 \end{pmatrix}. \end{aligned} \quad \dots (7c)$$

For evaluating (5) we substitute in it the values of photoionization amplitude, its Hermitian conjugate as well as (3), (6) and (7). The result can be simplified by analytically evaluating as many sums as possible present therein by applying Racah algebra. It requires, for example, the use of (a) the addition theorems from<sup>38</sup> for rotational and spherical harmonics, (b) Eq. (6.2.5)<sup>38</sup> for converting a single sum of the product of three 3-j symbols into a product of one 3-j and one 6-j symbols, (c) identity (5) given on page 453 in Ref.<sup>42</sup> for converting a single sum of the product of two 3-j symbols into a product of two 3-j and one 6-j symbols summed over two variables, (d) Eq.(14.42) from<sup>43</sup> which transforms a quadruple sum of the product of four 3-j symbols into a double sum containing two 3-j and one 6-j symbols, (e) Eq.(3.7.9)<sup>38</sup> for changing a phase factor into a 3-j symbol, (f) orthogonality (3.7.7)<sup>38</sup> of 3-j symbols.

The simplified form of EDM for angular distribution (EDMAD) in the process (1) in the absence of SOI can be written in the following form:

$$\begin{aligned} &\langle L_f S_f M_{S_f}; \mu \hat{u} \vec{k}_p | \rho^{SPI} | L_f S_f M'_{S_f}; \mu' \hat{u} \vec{k}_p \rangle \\ &= \frac{d^2 \sigma(m_r; JK_J M_J)}{d\hat{p} d\hat{k}_p} \sigma(S_0; S_f; \hat{u})_{M_{S_f} \mu; M'_{S_f} \mu'}, \end{aligned} \quad \dots (8)$$

where

$$\frac{d^2 \sigma(m_r; JK_J M_J)}{d\hat{p} d\hat{k}_p} = \frac{d^2 \sigma(m_r)}{d\hat{p} d\hat{k}_p} P_{JK_J M_J}(\beta) \quad \dots (9)$$

Here the term  $\frac{d^2 \sigma(m_r; JK_J M_J)}{d\hat{p} d\hat{k}_p}$  denotes the angular distribution (AD) of rotationally state selected and oriented molecule. Whereas the first term  $\frac{d^2 \sigma(m_r)}{d\hat{p} d\hat{k}_p}$

on the right-hand side of (9), describes the angular distribution of free gaseous molecule, can be written in the following form

$$\begin{aligned} \frac{d^2 \sigma(m_r)}{d\hat{p} d\hat{k}_p} &= (-1)^{L_0 + L_1 + m_r} \frac{K}{4(2L_0 + 1)} \\ &\sum_{\substack{p\tau hl \\ p'\tau h'l'}} \sum_{\lambda_r \lambda'_r M \Lambda_r L_r L L'} \sum_{L_r L L'} (-i)^{l-l'} \exp[i(l-l')] (2L_r + 1) \\ &\times (2L + 1)(2L' + 1)(2l + 1)^{1/2} (2l' + 1)^{1/2} \begin{pmatrix} l & l' & L_r \\ 0 & 0 & 0 \end{pmatrix} \\ &\times \begin{pmatrix} l & l' & L_r \\ -m & m' & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & L_r \\ m_r - m_r & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & L_r \\ -\lambda_r & \lambda'_r & \Lambda_r \end{pmatrix} \\ &\times \begin{Bmatrix} 1 & 1 & L_r \\ L' & L & L_0 \end{Bmatrix} \begin{Bmatrix} l & l' & L_r \\ L' & L & L_f \end{Bmatrix} b_{hlm}^{p\tau} b_{h'l'm'}^{p'\tau'*} \\ &\times \langle L_f, l | F_p | L_0, 1 \lambda_r \rangle \langle L_0, 1 \lambda'_r | F_p^\dagger | L_f, l' \rangle \\ &\times [Y_{L_r}^{-\Lambda_r}(\hat{p})]^* Y_{L_r}^M(\hat{k}) P_{L_r}(\cos \beta). \end{aligned} \quad \dots (10)$$

The coefficients  $b_{hlm}^{p\tau}$  are needed to form basis angular functions [also called generalized harmonics (GH)] which belong to the  $p$ th IR of dimensionality  $\tau$  of the molecular point group<sup>40,44</sup>. Finally  $\langle L_f, l | F_p | L_0, 1 \lambda_r \rangle$  with  $\lambda_r = 0$  and  $\pm 1$  are the photoionization amplitudes in the EI approximation. Substituting (7) and (10) in (9) and simplifying we obtain

$$\begin{aligned}
 \frac{d^2\sigma(m_r; JK_J M_J)}{d\hat{p}d\hat{k}_p} &= (-1)^{L_0+L_1+m_r} \frac{K}{8(2L_0+1)} \\
 &\times \sum_{\substack{p\tau hl \\ p'\tau'h'l'}} \sum_{\lambda_r\lambda_r'\Lambda_r} \sum_{L_r LL'} \sum_{nG} (-i)^{l-l'} \exp|i(l-l')| \\
 &\times (2L_r+1)(2L+1)(2L'+1)(2n+1)(2G+1) \\
 &\times (2l+1)^{1/2}(2l'+1)^{1/2} \begin{pmatrix} l & l' & L_r \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & L_r \\ -m & m' & 0 \end{pmatrix} \\
 &\times \begin{pmatrix} 1 & 1 & L_r \\ m_r - m_r & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & L_r \\ -\lambda_r & \lambda_r' & \Lambda_r \end{pmatrix} \begin{pmatrix} L_r & n & G \\ 0 & 0 & 0 \end{pmatrix}^2 \\
 &\times \begin{Bmatrix} 1 & 1 & L_r \\ L' & L & L_0 \end{Bmatrix} \begin{Bmatrix} l & l' & L_r \\ L' & L & L_f \end{Bmatrix} b_{hlm}^{p\tau} b_{h'l'm'}^{p'\tau'^*} \\
 &\times \langle L_f, l | F_p | L_0, 1\lambda_r \rangle \langle L_0, 1\lambda_r' | F_p^\dagger | L_f, l' \rangle \\
 &\times \bar{P}_n P_G(\cos\beta) [Y_{L_r}^{-\Lambda_r}(\hat{p})]^* Y_{L_r}^M(\hat{k}). \quad \dots (11)
 \end{aligned}$$

It is a positive quantity and acts as a multiplicative factor in the EDMAD in (8) for SPI process (1). The circular dichroism for angular distribution (CDAD) in photoionization of state select and oriented molecules is given by

$$\begin{aligned}
 \frac{d^2\sigma_{CD}(JK_J M_J)}{d\hat{p}d\hat{k}_p} &= \frac{d^2\sigma(m_r=+1; JK_J M_J)}{d\hat{p}d\hat{k}_p} - \frac{d^2\sigma(m_r=-1; JK_J M_J)}{d\hat{p}d\hat{k}_p} \\
 &= (-1)^{L_0+L_1+m_r} \frac{K}{8(2L_0+1)} \sum_{\substack{p\tau hl \\ p'\tau'h'l'}} \sum_{\lambda_r\lambda_r'\Lambda_r} \sum_{LL'} \sum_{nG} (-i)^{l-l'} \\
 &\times \exp|i(l-l')| (2L_r+1)(2L+1)(2n+1)(2G+1) \\
 &\times (2l+1)^{1/2}(2l'+1)^{1/2} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & L \\ -m & m' & \Lambda_r \end{pmatrix} \\
 &\times \begin{pmatrix} 1 & 1 & 1 \\ -\lambda_r & \lambda_r' & \Lambda_r \end{pmatrix} \begin{pmatrix} 1 & n & G \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} l & l' & 1 \\ L_r & L & L_0 \end{Bmatrix} \begin{Bmatrix} l & l' & 1 \\ L_r & L & L_f \end{Bmatrix} \\
 &\times b_{hlm}^{p\tau} b_{h'l'm'}^{p'\tau'^*} \langle L_f, l | F_p | L_0, 1\lambda_r \rangle \langle L_0, 1\lambda_r' | F_p^\dagger | L_f, l' \rangle \\
 &\times \bar{P}_n P_G(\cos\beta) [Y_1^{-\Lambda_r}(\hat{p})]^* Y_{L_r}^M(\hat{k}). \quad \dots (12)
 \end{aligned}$$

So, the EDM due to circular dichroism (EDMCD) for the process (1) in the absence of SOI can be written in the following form:

$$\begin{aligned}
 &\langle L_f S_f M_{S_f}; \mu \hat{u} \hat{k}_p | \rho_{CD}^{SPI} | L_f S_f M'_{S_f}; \mu' \hat{u} \hat{k}_p \rangle \\
 &= \frac{d^2\sigma_{CD}(JK_J M_J)}{d\hat{p}d\hat{k}_p} \sigma(S_0; S_f; \hat{u})_{M_{S_f}\mu; M'_{S_f}\mu'} \quad \dots (13)
 \end{aligned}$$

The first term present in right hand side of equation (13) is a positive quantity and acts as a multiplicative factor in the EDMCD. The second term (*i.e.*,  $\sigma(S_0; S_f; \hat{u})_{M_{S_f}\mu; M'_{S_f}\mu'}$ ) present on the right hand side of Eqs. (8) and (13) is the EDM for spin-correlation (EDMSC), completely determines the entanglement properties among electronic qubit ( $e_p$ ) and ionic qudit ( $M^+$ ), can be written as

$$\begin{aligned}
 \sigma(S_0; S_f; \hat{u})_{M_{S_f}\mu; M'_{S_f}\mu'} &= (-1)^{\mu+\mu'+M_{S_0}} \sum_{S_{qq'}} (2S+1) \\
 &\times \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ \mu - \mu' & q & \end{pmatrix} \begin{pmatrix} S_f & S_f & S \\ M_{S_f} & -M'_{S_f} & -q' \end{pmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ S_f & S_f & S_0 \end{Bmatrix} D_{qq'}^{S*}(\omega_u), \quad \dots (14)
 \end{aligned}$$

with  $\omega_u(\theta_u, \phi_u, 0)$ , the Euler angle which rotates the polar axis of the space-frame into the spin quantization direction  $\hat{u}$  (Fig. 1).

As a measure of the degree of entanglement, we consider the concurrence<sup>36,37</sup> which can be defined as

$$C = \left(2(1 - \text{Trace}\rho_A^2)\right)^{1/2} \quad \dots (15)$$

where  $\rho_A$  is the reduced density matrix.

### 3 Calculation of EDMSC between qudit and qubit system of rotationally state selected and oriented $C_{3v}$ molecule

Here we consider photoionization for the transition from  $a_1$  bound orbital of a state selected and oriented  $C_{3v}$  molecule. The group theoretical considerations show that one of the E1 transitions<sup>44</sup> is allowed in which the continuum orbital of the emitted photoelectron belongs to doubly degenerate  $E$  IR ( $a_1^2 \rightarrow e^{\frac{1}{2}}$ ), with  $p=1, h=1,$

$l=1, \tau=2$  and  $S_f = \frac{3}{2}$ . Moreover we have considered

here two experimental geometries for which the incident light is parallel [*i.e.*,  $\hat{p}(\theta_p=0, \phi_p)$ ] and perpendicular [*i.e.*,  $\hat{p}(\theta_p = \frac{\pi}{2}, \phi_p)$ ] to the weak and homogeneous orienting electric field  $\vec{E}$  in the OZ direction (Fig. 1).

### 3.1 Calculation for AD and CDAD

The expression for angular photo-current (11) for the transition described in previous paragraph when the incident light is parallel to the orienting electric field  $\vec{E}$  (parallel geometry) is given by

$$\begin{aligned} \frac{d^2\sigma(0;JK_J M_J)}{d\hat{p}(\theta_p=0,\phi_p)d\hat{k}} &\equiv \frac{d^+\sigma(0;JK_J M_J)}{d\hat{k}} \\ &= \frac{\sigma}{28\pi} \left[ 7\left(1 - \frac{1}{2}\bar{\beta} + \frac{3}{2}\bar{\beta}\cos^2\theta_k\right) + \right. \\ &\quad \left. \left\{ 14 - \frac{5}{14}(25 + 51\cos^2\theta_k)\bar{\beta} \right\} \bar{P}_2(JK_J M_J) + \right. \\ &\quad \left. \frac{18}{7}(3\cos^2\theta_k - 1)\bar{\beta}\bar{P}_4(JK_J M_J) + 6\left(\frac{6}{7}(7 - 5\bar{\beta})\bar{\beta}\right)^{1/2} \right. \\ &\quad \left. \times (\bar{P}_1(JK_J M_J) - \bar{P}_3(JK_J M_J))\cos\theta_k\sin\delta \right]. \quad \dots (16) \end{aligned}$$

Whereas for the incident light perpendicular to the orienting electric field  $\vec{E}$  (perpendicular geometry) the angular photo current becomes

$$\begin{aligned} \frac{d^2\sigma(0;JK_J M_J)}{d\hat{p}(\theta_p=\frac{\pi}{2},\phi_p)d\hat{k}} &\equiv \frac{d^+\sigma(0;JK_J M_J)}{d\hat{k}} \\ &= -\frac{\sigma}{28\pi} \left[ \frac{5}{2}\bar{\beta}\{(3\cos^2\theta_k - 4)\bar{P}_2(JK_J M_J) - \right. \\ &\quad \left. \frac{1}{2}\left\{ 3\left(\frac{7}{5} + \frac{10}{7}\bar{\beta} + \frac{6}{35}\bar{P}_4(JK_J M_J)\right)\sin^2\theta_k\cos 2(\phi_k - \phi_p) \right. \right. \\ &\quad \left. \left. - \left(\frac{7}{5} - \frac{10}{7}\bar{P}_2(JK_J M_J) + \frac{36}{35}\bar{P}_4(JK_J M_J)\right)(3\cos^2\theta_k - 1)\right\} \right. \\ &\quad \left. + 3\left(\frac{6}{7}(7 - 5\bar{\beta})\bar{\beta}\right)^{1/2} \{(\bar{P}_1(JK_J M_J) - \bar{P}_3(JK_J M_J))\cos\theta_k\sin\delta \right. \right. \\ &\quad \left. \left. - 7(1 - \bar{P}_2(JK_J M_J))\right\} \right]. \quad \dots (17) \end{aligned}$$

Where  $\sigma$ , the detection-integrated photoionization cross-section,  $\bar{\beta}$ , the angular asymmetry parameter and  $\delta$ , the Coulomb phase are all energy dependent quantities.

The CDAD given in Eq. (12), when the circularly polarized (CP) radiation is parallel to orienting electric field  $\vec{E}$ , becomes identically zero. That is

$$\frac{d^2\sigma_{CD}(JK_J M_J)}{d\hat{p}(\theta_p=0,\phi_p)d\hat{k}} \equiv \frac{d^+\sigma_{CD}(JK_J M_J)}{d\hat{k}} = 0 \quad \dots (18)$$

However if the CP photon beam incidents on the molecular target in a direction perpendicular to  $\vec{E}$ , the CDAD becomes

$$\begin{aligned} \frac{d^2\sigma_{CD}(JK_J M_J)}{d\hat{p}(\theta_p=\frac{\pi}{2},\phi_p)d\hat{k}} &\equiv \frac{d^+\sigma_{CD}(JK_J M_J)}{d\hat{k}} \\ &= \frac{3}{28\pi} \sigma \bar{P}_1(JK_J M_J) \left( \frac{15}{2}(7 - 5\bar{\beta})\bar{\beta} \right)^{1/2} \\ &\quad \times \sin\theta_k \sin(\phi_k - \phi_p) \cos\delta. \quad \dots (19) \end{aligned}$$

### 3.2 Bipartite Coulombic entanglement between ionic qudit and electronic qubit

The expression for EDMSC for rotationally state selected and oriented  $C_{3v}$  molecule can be calculated from (14) for the following two cases.

(i) When  $S_0 = S_f - \frac{1}{2}$  with  $S_f = \frac{3}{2}$ , the EDMSC,  $\sigma(S_0; S_f; \hat{u})_{M_{S_f \mu}; M'_{S_f \mu}}$ , is given in Table 1.

The eigenvalues of EDMSC calculated from Table 1 are  $\left\{ \frac{1}{3}, \frac{1}{3}, \frac{1}{3}, 0, 0, 0, 0, 0 \right\}$ . These eigenvalues are independent of the spherical angles  $(\theta_u, \phi_u)$  specifying the spin quantization direction  $\hat{u}$ . We also find that the EDMSC in Table 1 has more than one nonzero eigenvalues which suggest that all the states for  $S_f = \frac{3}{2}$  are mixed states<sup>45</sup>.

For measuring the degree of entanglement, we have calculated the concurrence using Table 1 according to the definition given in (15) which yields

$$C = \left( \frac{1}{8} \left( 7 - \frac{5\cos^2\theta_u}{9} \right) \right)^{1/2} \quad \dots (20)$$

The variation of concurrence with  $\theta_u$  is shown in Fig. 2. Fig. 2 shows that the system is entangled (free entanglement) for all values of  $\theta_u$ .

(ii) When  $S_0 = S_f + \frac{1}{2}$  with  $S_f = \frac{3}{2}$ , the value of the square of the concurrence becomes negative and does not show the free entanglement. Horodecki *et al.*<sup>33</sup> have shown that though a system may not obey the condition for free entanglement it may have bound



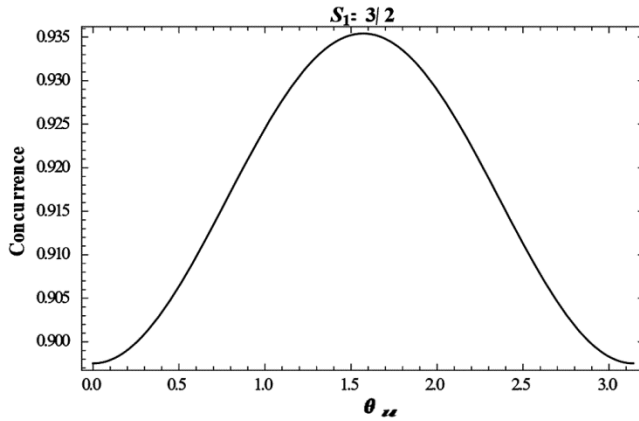


Fig. 2 — Variation of EDMSC Concurrence with spin quantization direction ( $\theta_u$ ).

entanglement if the dimension of the Hilbert space is more than six and obeys the inequality condition written below

$$\text{Rank}[\sigma(S_0 = S_f + \frac{1}{2}; S_f = \frac{3}{2})] \geq \text{Max} \{ \text{Rank}[\sigma(e_p)], \text{Rank}[\sigma(M^+)] \} \quad \dots (21)$$

Here,  $\text{Rank}[\sigma(S_0 = S_f + \frac{1}{2}; S_f = \frac{3}{2})]$  is  $2(2S_f + 1) = 8$ ,

$\text{Rank}[\sigma(e_p)] = 2$  and  $\text{Rank}[\sigma(M^+)]$  is  $(2S_f + 1) = 4$ . So, the state  $S_0 = S_f + \frac{1}{2}$  with  $S_f = \frac{3}{2}$  obeys the condition (21) and hence possesses bound entanglement.

#### 4 Results and Discussion

In this section, we present our results of the calculations developed in section 3 of this paper for photoionization from  $13a_1^2$  orbital of a single  $|JK_J M_J\rangle$  rotational state of an oriented gaseous  $\text{CH}_3\text{I}$  molecule. In our study we have used photon energy of 16 eV reported by Carson *et al.*<sup>46</sup> corresponding to  $\sigma = 15.5$  Mb and  $\bar{\beta} = 0.28$  in the process (1) of the photoelectrons emitted with energy 3.5 eV. Also we have considered  $1 \leq J \leq 5$  appropriate for low-temperature beams.

Using equations (8), (16) and (20), the concurrence of EDM for angular distribution (EDMAD) in photoionization of  $\text{CH}_3\text{I}$  for the values of  $\phi_k = \phi_p$  and  $\delta = \frac{\pi}{2}$  in case of parallel geometry becomes

$$C^\perp(0;111) = 0.1226(5.47 + 2.76\cos\theta_k - \cos^2\theta_k) \times (1 - 0.794\cos^2\theta_u)^{1/2}, \quad \dots (22a)$$

where  $|JK_J M_J\rangle = |111\rangle$  and

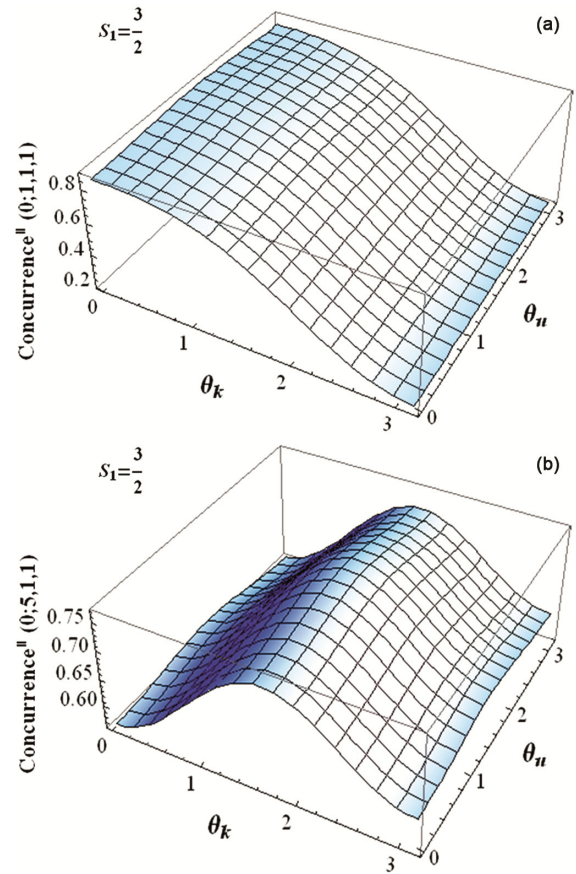


Fig. 3 — Variation of EDMAD Concurrence for parallel geometry [for  $|JK_J M_J\rangle = |111\rangle$  (a) and for  $|JK_J M_J\rangle = |511\rangle$  (b) with respect to  $\theta_k$  and  $\theta_u$ .

$$C^\perp(0;511) = 0.155(4.84 - 0.167\cos\theta_k - \cos^2\theta_k) \times (1 - 0.794\cos^2\theta_u)^{1/2} \quad \dots (22b)$$

where  $|JK_J M_J\rangle = |511\rangle$ .

Similarly for perpendicular geometry, using equations (8), (17) and (20), the concurrence for EDMAD is given by

$$C^\perp(0;111) = 0.0803(12.329 - 0.888\cos\theta_k - \cos^2\theta_k) \times (1 - 0.794\cos^2\theta_u)^{1/2} \quad \dots (23a)$$

for  $|JK_J M_J\rangle = |111\rangle$

and

$$C^\perp(0;511) = 0.0183(43.71 + 0.3\cos\theta_k - 0.58\cos^2\theta_k) \times (1 - 0.794\cos^2\theta_u)^{1/2} \quad \dots (23b)$$

for  $|JK_J M_J\rangle = |511\rangle$ .

From Figs 3 & 4 we see that nature of variations as well as magnitudes of concurrence (*i.e.* entanglement)



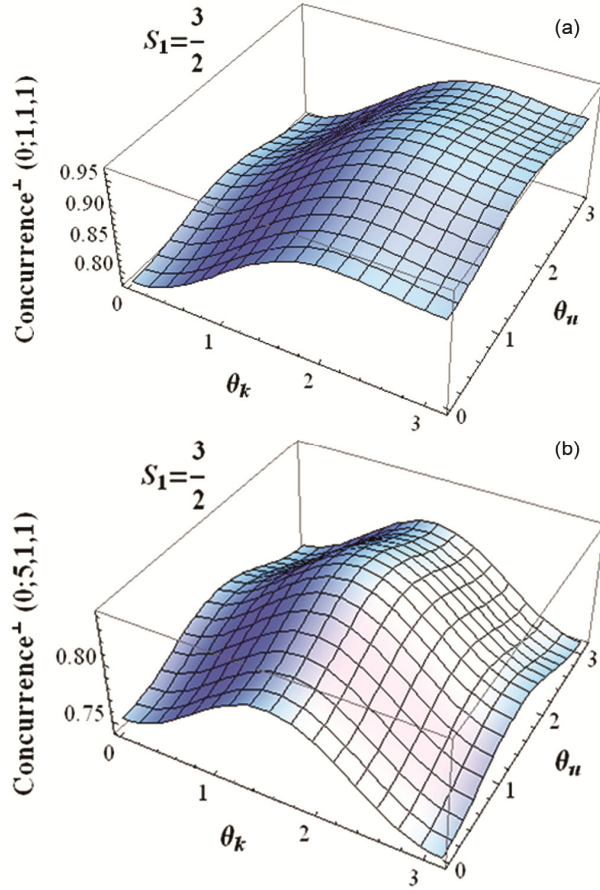


Fig. 4 — Variation of EDMCD Concurrence for perpendicular geometry [for  $|JK_J M_J\rangle = |111\rangle$  (a) and for  $|JK_J M_J\rangle = |511\rangle$  (b)] with respect to  $\theta_k$  and  $\theta_u$ .

depend on the direction of incident photon beam, of ejection of photoelectrons along with their spin-polarization and also on the rotational states of gaseous  $\text{CH}_3\text{I}$  molecule. R. B. Bernstein and his group<sup>25</sup> performed experimental measurement for AD of photoionization of state selected and oriented  $\text{CH}_3\text{I}$  molecule. This experimental technique can equally be applied for the measurement of EDMAD in our present case of  $\text{CH}_3\text{I}$  molecule.

The equation (18) shows that the value of CD in case of parallel geometry becomes zero and consequently the concurrence of EDM circular dichroism (EDMCD) in this case will also be zero. Using equations (13), (19) and (20), the concurrence for EDMCD in photoionization of  $\text{CH}_3\text{I}$  molecule in case of perpendicular geometry, where the values of

$$\phi_k - \phi_p = \frac{\pi}{2} \text{ and } \delta = 0, \text{ yields}$$

$$C_{CD}^{\perp}(0;111) = 0.933 \sin \theta_k \left(1 - 0.794 \cos^2 \theta_u\right)^{1/2},$$

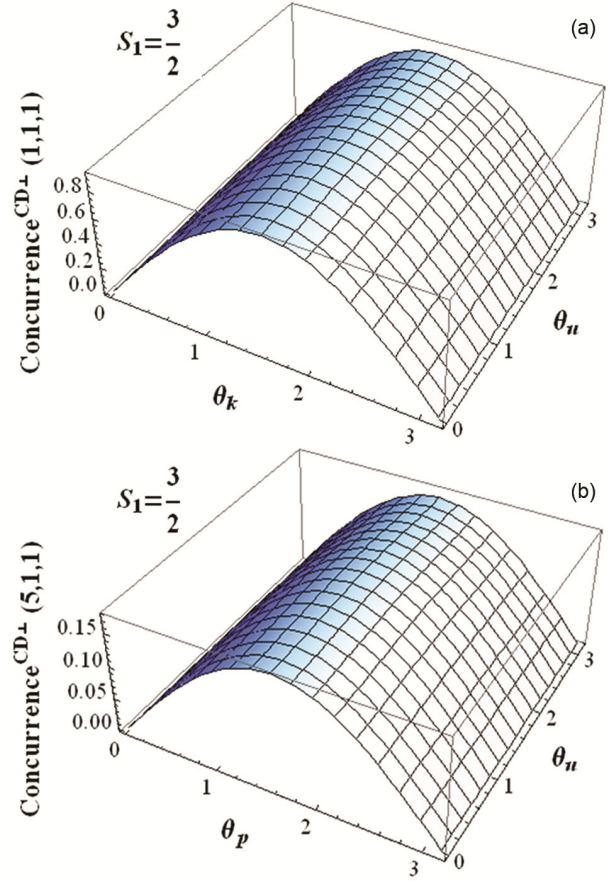


Fig. 5 — Variation of EDMCD Concurrence for perpendicular geometry [for  $|JK_J M_J\rangle = |111\rangle$  (a) and for  $|JK_J M_J\rangle = |511\rangle$  (b)] with respect to  $\theta_k$  and  $\theta_u$ .

when  $|JK_J M_J\rangle = |111\rangle$

and

$$C_{CD}^{\perp}(0;511) = 0.179 \sin \theta_k \left(1 - 0.794 \cos^2 \theta_u\right)^{1/2}, \dots \quad (24)$$

when  $|JK_J M_J\rangle = |511\rangle$ .

From Figs (3), (4) & (5) we find that the natures of concurrences (*i.e.*, entanglement measurement) are different for EDMAD and EDMCD for rotationally state selected and oriented gaseous  $\text{CH}_3\text{I}$  molecule. It is also observed from Fig. (5) that though the natures of variations of EDMCD concurrences are same, their magnitudes differ for different rotational states in photoionization of  $\text{CH}_3\text{I}$  molecule. C. Westphal *et al.*<sup>31</sup> have performed CDAD measurements for the oriented  $\text{CH}_3\text{I}$  molecule. The same experimental techniques can also be used to observe the EDMCD effect of  $\text{CH}_3\text{I}$  molecule, state selected and oriented through electrostatic Hexapole field method<sup>25</sup>.

## 5 Conclusion

High-dimensional quantum entanglement is currently a great interest of research as it can enable higher encoding efficiency in quantum communication protocols, such as quantum key distribution and quantum teleportation. Photoionization is a simple natural process and has played a very important role in the development of quantum mechanics. In this article we have introduced a scheme for generation of qudit-qubit entanglement by using the method of photoionization in rotationally state selected, oriented  $C_{3v}$  molecules. The entanglement is quantified by concurrence. A quantitative application has been considered for the bipartite case in photoionization from  $13a_1^2$  orbital of a rotationally state selected oriented  $CH_3I$  molecule. This bipartite system may be in mixed states and may possess free or bound entanglement. The qudit-qubit system can be either totally entangled or partially entangled or separable depending on the spin states of target  $M$  and residual ion  $M^+$  as well as of the direction of incidence of photon beam along with its polarization, of spin quantization and of ejection of the photoelectrons. It is also observed that rotational state of the target molecule and circular dichroism have significant effects on the entangled properties of the system.

## Authors' Contributions

Both authors contributed equally to this work.

## Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Conflict of Interest

The authors have no conflicts to disclose.

## References

- Bell J S, *Physics*, 1 (1965) 195.
- Nielsen M A & Chuang I L, *Quantum computation and quantum information*, (Cambridge University Press Cambridge, England) 2010.
- Bouwmeester D, Ekert A K & Zeilinger A, *The physics of quantum information, quantum cryptography*, (Springer Berlin) 2013.
- Alber G, Berth T, Horodecki M, Horodecki P, Horodecki R, Rötteler M, Weinfurter H, Werner R & Zeilinger A, *An introduction to basic theoretical concepts and experiments*, (Springer Berlin) 2000.
- Mitchell M W, Lundeen J S & Steinberg A M, *Nature*, 429 (2004) 161.
- Boto A N, Kok P, Abrams D S, Braunstein S L, Williams C P & Dowling J P, *Phys Rev Lett*, 85 (2000) 2733.
- Galindo A & Martin-Delgado M A, *Rev Mod Phys*, 74 (2002) 347.
- Islam N T, High-rate, high-dimensional quantum key distribution systems (Springer Nature Switzerland) 2018.
- Parida S & Chandra N, *Phys Rev A*, 79 (2009) 062501.
- Bechmann-Pasquinucci H & Peres A, *Phys Rev Lett*, 85 (2000) 3313.
- Chandra N & Ghosh R, *Quantum entanglement in electron optics*, (Springer-Verlag Berlin) 2013.
- Brukner C, Zukowski M & Zeilinger A, *Phys Rev Lett*, 89 (2002) 197901.
- Vaziri A, Pan J W, Jennewein T, Weihs G & Zeilinger A, *Phys Rev Lett*, 91 (2003) 227902.
- Babazadeh A, Erhard M, Wang F, Malik M, Nouroozi R, Krenn M & Zeilinger A, *Phys Rev Lett*, 119 (2017) 180510.
- Shen S Q, Liang J M, Li M, Yu J & Fei S M, *Phys Rev A*, 101 (2020) 012312.
- Lee C K, Najafabadi M S, Schumayer D, Kwek L C & Hutchinson D A W, *Sci Rep*, 9 (2019) 9147.
- Parida S & Chandra N, *Phys Rev A*, 86 (2012) 062302.
- Chakraborty M & Sen S, *J Electron Spectrosc Relat Phenom*, 203 (2015) 60.
- Chakraborty M & Sen S, *Trans Mach Learn Artific Intel*, 7 (2019) 1.
- Chandra N & Ghosh R, *Phys Rev*, 69 (2004) 012315.
- Chandra N & Ghosh R, *Radiat Phys Chem*, 75 (2006) 1808.
- Ghosh R, Chandra N & Parida S, *Eur Phys J Special Topics*, 169 (2009) 117.
- Sen S & Chakraborty M, *Pramana – J Phys*, 94 (2020) 125.
- Chandra N & Chakraborty M, *J Chem Phys*, 95 (1991) 6382.
- Kramer K H & Bernstein R B, *J Chem Phys*, 42 (1965) 767.
- The word 'Orientation' in this article always means the relation between the molecular geometry and some reference axis.
- Cherepov N A & Kuznetsov V V, *J Phys B*, 20 (1987) L159.
- Cherepov N A & Kuznetsov V V, *Z Phys D*, 7 (1987) 271.
- Chandra N, *Phys Rev A*, 39 (1989) 2256.
- Chandra N & Chakraborty M, *Eur Phys J D*, 2 (1998) 253.
- Westphal C, Bansmann J, Getzlaff M, Schinhense G, Cherepov N A, Braunstein M, McKay V & Dubs R L, *Surface Science*, 253 (1991) 205.
- Peres A, *Phys Rev Lett*, 77 (1996) 1413.
- Horodecki M, Horodecki P & Horodecki R, *Rev Mod Phys*, 81 (2009) 865.
- Horodecki M, Horodecki P & Horodecki R, *Phys Rev A*, 223 (1996) 1.
- Horodecki M, Horodecki P & Horodecki R, *Phys Rev Lett*, 80 (1998) 5239.
- Rungta P, Bužek V, Caves C M, Hillery M & Milburn G Z, *Phys Rev A*, 64 (2001) 042315.
- Rai S & Luthra J R, *arXiv:quant-ph/0508045v1* 5 Aug 2005.
- Edmonds A R, *Angular momentum in quantum Mechanics*, (Princeton University press Princeton) 2016.
- Breit G & Bethe H A, *Phys Rev*, 93 (1954) 88.
- Chandra N, *Chem Phys*, 102 (1986) 179.
- Zare R N, Kleiman V D & Park H, *Angular momentum: Understanding spatial aspects in chemistry and physics and companion to angular momentum* (Wiley) 1998.

- 42 Varshalovich D A, Moskalev A N, & Khersonskii V K, Quantum theory of angular momentum (World Scientific Singapore) 1989.
- 43 De-Shalit A & Talmi I, Nuclear shell theory: Pure and applied Physics, V14 (Literary Licensing, LLC) 2013.
- 44 Chandra N, *J Phys B*, 20 (1987) 3405.
- 45 Blum K, Density matrix theory and applications (Springer-Verlag Berlin and Heidelberg GMBH & Co. K) 3rd Edn, 2012.
- 46 Carlson T A, Fahman A, Krause M O, Keller P R, Taylor J W, Whiteley T & Grimm F A, *J Chem Phys*, 80 (1984) 3521.