

# EPR Breakup of Polyatomic Molecules<sup>†</sup>

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We explore the EPR experiment in the case of the breakup of a polyatomic molecule into two mutually entangled fragments. We give a derivation based on the properties of the dissociated wave function that no information is transferred, not even at a speed smaller than the speed of light, from one entangled partner to the other concerning its measurement or lack thereof. We also explain experiments that show that each separated fragment can retain coherences induced in its parent molecule by a broad band laser pulse, regardless of whether a measurement has been performed on its entangled partner.

## I. Introduction

In their famous paper,<sup>1</sup> Einstein, Podolski, and Rosen (EPR) pointed out that a necessary consequence of quantum mechanics is the establishment of correlations between two entangled particles dissociated from the same initial adduct. Thus, if the total spin of the adduct is zero, a choice of quantization axis upon measurement of one fragment would yield a spin which is the exact opposite of the spin measured for the other fragment but only when the same axis of quantization is chosen in both measurements. The issue is how can one fragment be “aware” of the choice made regarding the quantization axis of the other?

Although the existence of these correlations has been established experimentally,<sup>2,3</sup> it has however been argued on the basis of causality<sup>4</sup> that no “spooky interaction at a distance” nor any information can be transferred between the fragments as a sole result of a measurement being performed on either fragment. Were it to be the case, we would be able to transfer information at speeds greater than that of light. Only when the two observers get together, or send each other the details of their measurements by any other ordinary “classical” communication channel, do they become aware of the existence of these correlations.

It is of interest to see whether the above heuristic argument can also be derived directly from the Schrödinger equation, and more explicitly, from the properties of its solutions. It is also of interest to see whether any information, even at sub-light speeds, which is not forbidden by causality, can be transferred between the fragments as a result of observations performed on one of them.

In this paper, we address these issues by analyzing the EPR dissociation of a case more complicated than those considered so far, that of a polyatomic molecule breaking apart under the action of a broad or narrow band light pulse to yield two fragments. Here, because of the presence of both discrete and continuous variables, the collapse of the wave function upon measurement is even more dramatic than in the two particle case and would seem to enable an observer of one fragment to sense when an observation of the other fragment is being made. This however, as we show below, is not the case.

## II. Multichannel Photodissociation

Consider irradiating a polyatomic molecule, A–B, where A and B are atoms or groups of atoms, existing initially in state  $\Psi_0$  of energy  $E_0$ , with a pulse of light of the form

$$E_1(t) = R_e \int dE \epsilon_1(\omega_E) \exp(-i\omega_E t) \quad (1)$$

where  $E$  is an energy value in the continuum and  $\omega_E = E - E_0$ , with a.u., for which  $\hbar = 1$ , being used here and throughout this paper. After the pulse is over, those molecules that have absorbed a photon from the pulse and are on their way to yield the A + B fragments are described<sup>5</sup> by the following wave function

$$\Psi_1(\mathbf{R}, \mathbf{r}, t) = \int dE \sum_n c_n^{(1)}(E) \psi^{(-n)}(\mathbf{R}, \mathbf{r}, E) \exp(-iEt) \quad (2)$$

where  $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$ , with  $\mathbf{R}_A$  and  $\mathbf{R}_B$  denoting, respectively, the lab-frame coordinates of A (c.m.) and B (c.m.). In the above,  $\mathbf{r}$  is a collective index for the B fragment internal coordinates and  $n$  stands for  $\{v, \hat{\mathbf{k}}\}$ , where  $v$  is the collective quantum number for the internal motions of B and  $\hat{\mathbf{k}}$  is the direction angles of  $\mathbf{k}$ , the momentum conjugate to  $\mathbf{R}$ .  $\sum_n$  designates summation over  $v$  and integration over  $\hat{\mathbf{k}}$ .

$\psi^{(-n)}(\mathbf{R}, \mathbf{r}, E) \exp(-iEt)$  are scattering solutions<sup>6</sup> of the full time independent Schrödinger equation

$$\lim_{\epsilon \rightarrow +0} (E - i\epsilon - H) \psi^{(-n)}(\mathbf{R}, \mathbf{r}, E) = 0 \quad (3)$$

which approach at large  $t$  a single product of an internal wave function of B and a plane wave in  $\mathbf{R}$ , function

$$\psi^{(-n)}(\mathbf{R}, \mathbf{r}, E) \exp(-iEt) \xrightarrow{t \rightarrow \infty} N(k_v(E)) \phi_v(\mathbf{r}) \exp[i\mathbf{k}_v(E) \cdot \mathbf{R} - iEt] \quad (4)$$

where  $\mathbf{k}_v(E)$  is the “channel-momentum” vector whose magnitude is determined by energy conservation to be

$$\frac{k_v^2(E)}{2\mu} = E - e_v \quad (5)$$

In the above,  $e_v$  is the energy of the  $\phi_v$  B state and  $\mu$  is the

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(A–B) reduced mass, defined as

$$\frac{1}{\mu} = \frac{1}{m(A)} + \frac{1}{m(B)}$$

that is

$$\mu = \frac{m(A)m(B)}{m(A) + m(B)} \quad (6)$$

$N(k)$  is a normalization constant that guarantees that

$$\int d\mathbf{R} |N(k)|^2 \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}] = \delta(E - E') \delta(\hat{\mathbf{k}} - \hat{\mathbf{k}}') \quad (7)$$

that is

$$N(k) = (\mu k / (2\pi)^3)^{1/2} \quad (8)$$

$c_n^{(1)}(E)$  of eq 2 are preparation coefficients, given in first-order perturbation theory as

$$c_n^{(1)}(E) = 2\pi i \epsilon_1(\omega_E) \langle \psi^{(-n)}(E) | d_1 | \psi_0 \rangle \quad (9)$$

where  $d_1$  is the transition dipole operator in the direction of the electric field  $E_1$ .

### III. Nondegenerate Case

**III.1. Collapsed Wave Function.** It follows from eq 5 that, if the B fragment has no degeneracies and A is assumed to be a structureless atom, knowledge of  $E$  and determination of  $k_v(E)$  (which can be performed by measuring atom A only) completely determines which  $e_v$  level of B is occupied, thereby causing the collapse of the wave packet of eq 2 to one term only.

Before discussing this further, we verify that  $k_v(E)$  can be determined by measuring A alone. We note that, if we assume that the total c.m. momentum  $K_{A-B} = 0$ , we have that

$$\mathbf{k}_v^A = -\mathbf{k}_v^B \quad (10)$$

Since

$$\mathbf{k}_v(E) = \mu(\mathbf{v}_v^A - \mathbf{v}_v^B)$$

we have that

$$\mathbf{k}_v(E) = \mathbf{k}_v^A = -\mathbf{k}_v^B \quad (11)$$

The above implies that as we measure  $k_v(E)$ , the wave function, which in the far future is given, using eq 4, as

$\Psi_1(\mathbf{R}, \mathbf{r}, t) \rightarrow$

$$\sum_n \int dE c_n^{(1)}(E) \phi_v(\mathbf{r}) N(k_v(E)) \exp[i\mathbf{k}_v(E) \cdot \mathbf{R} - iEt] \quad (12)$$

must collapse to a single term

$\psi_n(\mathbf{R}, \mathbf{r}, t) =$

$$\int dE c_n^{(1)}(E) \phi_v(\mathbf{r}) N(k_v(E)) \exp[i\mathbf{k}_v(E) \cdot \mathbf{R} - iEt] \quad (13)$$

As we repeatedly measure A and bin these measurements according to their different  $k_v(E)$  values, the system is described by a density matrix of the form

$$\rho = \sum_n |\psi_n\rangle \langle \psi_n| \quad (14)$$

with  $\psi_n$  being the “collapsed” wave function of eq 13. In the

CW case where

$$c_n^{(1)}(E) = c_n^{(1)}(E_0) \delta(E - E_0)$$

we have that

$$\rho(\mathbf{r}) = \sum_v \int d\hat{\mathbf{k}} |c_{v,\hat{\mathbf{k}}}^{(1)}(E_0) \phi_v(\mathbf{r})|^2 \quad (15)$$

**III.2. Uncollapsed Wave Function.** We can write the uncollapsed wave function as a sum of products of internal and translational wave functions

$$\Psi_1(\mathbf{R}, \mathbf{r}, t) = \sum_n \int dE c_n^{(1)}(E) \phi_v(\mathbf{r}) \psi_n(\mathbf{R}, E) \exp(-iEt) \quad (16)$$

where

$$\psi_n(\mathbf{R}, E) = N(k_v(E)) \exp(i\mathbf{k}_v(E) \cdot \mathbf{R}) \quad (17)$$

When we lack knowledge of A, the probability-density of B associated with this wave function is obtained by squaring this expression and integrating over the relative translational coordinate  $\mathbf{R}$

$$\rho_B = \int_V d\mathbf{R} |\Psi(\mathbf{R}, \mathbf{r}, t)|^2 = \sum_{n,n'} dE dE' G_{n,n'}(E, E') c_n(E) c_{n'}^*(E') \phi_v(\mathbf{r}) \phi_{v'}^*(\mathbf{r}) \exp[i(E' - E)t] \quad (18)$$

where

$$G_{n,n'}(E, E') \equiv \int_V d\mathbf{R} \psi_n^*(\mathbf{R}, E') \psi_n(\mathbf{R}, E) = \int_V d\mathbf{R} N(k_v(E)) N(k_{v'}(E')) \exp[i(\mathbf{k}_v(E) - \mathbf{k}_{v'}(E')) \cdot \mathbf{R}] = N(k_v(E)) N(k_{v'}(E')) \frac{8 \sin(\Delta k_x X) \sin(\Delta k_y Y) \sin(\Delta k_z Z)}{\Delta k_x \Delta k_y \Delta k_z} \quad (19)$$

where  $V$  is a limited volume of separation between the A and B fragments.

At  $R \gg 1/\Delta k$  values, terms with  $\Delta k \neq 0$  decay to zero and the probability-density becomes that of the collapsed case. Before dealing with the limited  $V$  case further, we examine the case in which the separation between A and B is allowed to assume any value. We then obtain from eq 19 that

$$G_{n,n'}(E, E') = N(k_v(E))^2 \delta(k_v(E) - k_{v'}(E')) \delta(\hat{\mathbf{k}}_v(E) - \hat{\mathbf{k}}_{v'}(E')) \quad (20)$$

hence

$$\rho_B = \sum_{v,v'} \int dE \int d\hat{\mathbf{k}} c_{v,\hat{\mathbf{k}}}(E) c_{v',\hat{\mathbf{k}}}'^*(E') \phi_v(\mathbf{r}) \phi_{v'}^*(\mathbf{r}) \exp[i(e_{v'} - e_v)t] \quad (21)$$

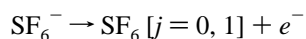
where

$$k_v(E) = k_{v'}(E')$$

or

$$E' = E - e_v + e_{v'} \quad (22)$$

As a real example, we consider the photodetachment of  $\text{SF}_6^-$



where  $j$  designates the  $\text{SF}_6$  angular momentum. The internal states we wish to consider are split by twice the rotational constant, i.e.

$$\Delta e \sim 3 \text{ cm}^{-1} = 1.37 \times 10^{-5} \text{ a.u.}$$

This means that  $\Delta k$  may be calculated as follows:

$$\Delta e = (k_v^2 - k_{v'}^2)/2\mu$$

Assuming that the average kinetic energy of the ejected electron is  $\bar{E}_k$

$$\bar{k}^2/2\mu = \bar{E}_k$$

that is

$$\bar{k} = (2\mu\bar{E}_k)^{1/2}$$

and since we have that

$$\Delta e \approx (k_v - k_{v'})2\bar{k}/2\mu = \Delta k\bar{k}/\mu = \Delta k(2\bar{E}_k/\mu)^{1/2}$$

we have that

$$\Delta k = (\mu/(2\bar{E}_k))^{1/2}\Delta e$$

Performing photodetachment at  $E_k = 1 \text{ eV} = 1/27 \text{ a.u.}$  and given that for  $e^- \mu \approx 1 \text{ a.u.}$ , we have that

$$\Delta k = (27/2)^{1/2}(1.37 \times 10^{-5}) = 5 \times 10^{-5}$$

This means that the probability-density, measured by say, laser induced fluorescence (LIF), must be collected over a volume-element whose linear dimension is

$$\Delta X < 2 \times 10^4 \text{ a.u.} \approx 1 \mu\text{m}$$

for the modulations of eq 16 not to be averaged out so that the signature of the uncollapsed wave packet of eq 16 could be established.

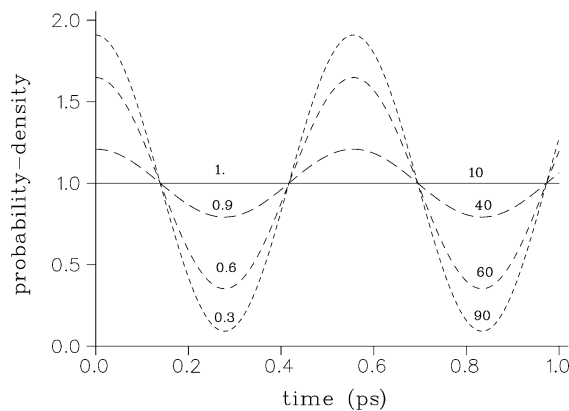
In fact, the signature of the uncollapsed wave packet can never be established in this way. To see this, we re-expressed the above estimate in terms of  $\Delta\tau$ , the measurement time over which we are still aware of the difference between the collapsed and uncollapsed wave packets.

$$\Delta\tau = \frac{\Delta X}{v} = \frac{1}{\Delta k \cdot v} = \frac{1}{\Delta e} \quad (23)$$

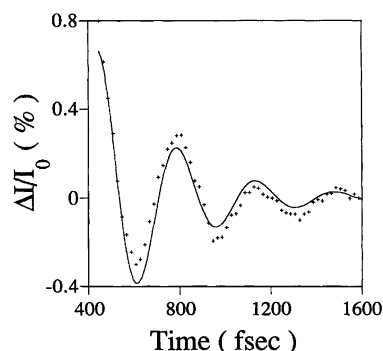
However, a pulse of duration  $\Delta\tau$  has bandwidth of  $1/\Delta\tau$  which by eq 23 =  $\Delta e$ . As we show below when the pulse bandwidth exceeds  $\Delta e$  it is not possible for us to be aware of the measurement of  $\mathbf{k}_A$  by measuring B!

**III.2.1. Large Bandwidth Excitation-Pulse Case.** To maintain (vibrational) coherence of the B fragment we must have contributions from  $v \neq v'$  terms of eq 22. This can be realized only when both  $c_{v,\hat{\mathbf{k}}}(E)$  and  $c_{v',\hat{\mathbf{k}}}(E')$  are nonnegligible for  $E$  and  $E'$  that satisfy eq 22, namely the  $E_1(t)$  pulse width must be larger than the vibrational spacing  $\Delta e = |e_v - e_{v'}|$ . In that case<sup>7,8</sup> knowledge of  $k_v(E)$  as obtained from measurements performed on A does not tell us which vibrational state is occupied by B, since it is possible for  $k_v(E)$  to be equal to  $k_{v'}(E')$ .

The effect of the loss of “which way” information<sup>9,4,10</sup> on the observed coherence of the wave packet of B is illustrated



**Figure 1.** Modulation of the probability-density according to 12 as a function of the dissociating pulse-width. The “which-way” parameter, ( $w_{v,v'} \equiv |c_v - c_{v'}|$ ) ranging from 1 for a narrow band pulse ( $\Delta = 10 \text{ cm}^{-1}$ ) to 0.3 for a broad-band pulse ( $\Delta = 90 \text{ cm}^{-1}$ ) indicates the degree of “which way” information we have when we measure  $k_v(E)$ .

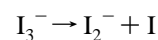


**Figure 2.** Modulation in the  $\text{I}_2^-$  pump-probe signal resulting from the short pulse dissociation of  $\text{I}_3^- \rightarrow \text{I}_2^- + \text{I}$ . Taken from ref 11.

in Figure 1. We show there how temporal modulations develop as we increase the bandwidth of the  $E_1(t)$  dissociation laser. Simultaneously with the increase in the laser’s bandwidth, we progressively lose information concerning the  $v \leftrightarrow k_v(E)$  correspondence, as other  $E'$  energies, for which  $k_v(E) = k_{v'}(E')$ , begin to contribute significantly to the B probability-density.

Plotted also is the “which-way” parameter, ( $w_{v,v'} \equiv |c_v - c_{v'}|$ ) which ranges from 1 for the CW case, in which we have full “which-way” information regarding the vibration  $\leftrightarrow$  translation correspondence, to 0, for an ultra broad-band pulse for which  $c_v \sim c_{v'}$ , resulting in the loss of the vibration  $\leftrightarrow$  translation “which-way” information.

In Figure 2, we plot the temporal modulations observed<sup>11</sup> in  $\text{I}_2^-$  resulting from the



photodissociation process. The experiment is done in the condensed phase with the momenta of the translational motion never measured. Nevertheless, as predicted in eq 22, coherence of the  $\text{I}_2^-$  fragment is observed and is being maintained for relatively long times (until relaxation sets in).

When the “which-way” parameter is 1 (e.g., for CW excitation) eq 22 only holds when  $v = v'$  (hence when  $E = E'$ ), and we have that

$$\rho_B = \sum_v \int d\hat{\mathbf{k}} |c_{v,\hat{\mathbf{k}}}(E) \phi_v(\mathbf{r})|^2 \quad (24)$$

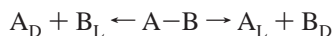
an expression that is indistinguishable from the collapsed case (CW). We see that in either, CW or ultrashort pulse, case, no

information is conveyed about the measurement, or lack thereof, from one fragment to its entangled partner.

#### IV. Degenerate Case

In the previous section, we saw that the lack of information transfer between A and B is due to the cancellation of the interference terms associated with different  $k_v(E)$  values upon integration over the A–B distance. Since the difference in  $k_v(E)$  values is due to the nondegeneracy of the internal energy  $e_v$  of the B fragment, it is of interest to investigate whether information transfer would be possible if the  $e_v$  values were degenerate.

In the degenerate case, we would need to find another marker to distinguish between the fragment channels, since  $k_v(E)$  are the same for all degenerate fragment states. Such a marker can be provided if one or both fragments are chiral. We consider therefore the photodissociation of an A–B molecule made up of A and B chiral fragments. Each fragment has a right-handed, denoted *D*, optical-isomer and a left-handed, denoted *L*, optical-isomer. Assuming that the adduct A–B has no handedness, and since handedness is conserved, the photodissociation of A–B can only result in the following two outcomes



Because of the degeneracy in the D and L fragment states, the uncollapsed wave function can be written in the CW case as

$$|\Psi_I(\mathbf{R}, t)\rangle = \psi(\mathbf{R}, E) \exp(-iEt) \{c_{D,L}|A_D\rangle|B_L\rangle + c_{L,D}|A_L\rangle|B_D\rangle\} \quad (25)$$

where  $c_{D,L}$  and  $c_{L,D}$  are preparation coefficients analogous to  $c_n^{(1)}(E)$  of the previous section, and

$$\psi(\mathbf{R}, E) = N(k) \exp(ik(E) \cdot \mathbf{R}) \quad (26)$$

is a translational wave function which, because of degeneracy, is common to all of the internal states of the fragments. It is clear that averaging over  $\mathbf{R}$  as performed on  $\rho_B$  of 10 will not kill the interference term because in this case  $|\psi(\mathbf{R}, E)|^2 = N(k)^2$  is independent of  $\mathbf{R}$ . It is also clear that a measurement of the handedness of A will immediately collapse the handedness of B.

We can now ask whether an observer at say B can differentiate between the uncollapsed and collapsed wave function, not knowing whether measurement on A has been done. For example, we can look at whether a certain optical transition is allowed or not. If we start from a symmetric wave function of A–B, we know that for an electric-dipole allowed transition only transitions to an antisymmetric wave function are possible. In contrast, since, per definition, the chiral fragments lack a center of symmetry, the above selection rule does not apply to them. This can also be seen in the following way: Each chiral state can be written as a superposition of a symmetric and antisymmetric states

$$|D\rangle = |A\rangle + |S\rangle, |L\rangle = |A\rangle - |S\rangle \quad (27)$$

Thus, each chiral state contains both a symmetric and an antisymmetric component, hence transitions to both  $|A\rangle$  and  $|S\rangle$  excited states are allowed.

Thus the question is whether the entangled dissociated state of eq 25 retains the symmetry property of the original wave function of A–B (in which case an observer at B will be able to distinguish between the collapsed and uncollapsed wave function), or not.

To answer this question the observer at the B position irradiates the B fragment by a second pulse of the form

$$E_2(t) = R_e \epsilon_2 \exp(-i\omega_2 t) \quad (28)$$

where  $\omega_2 = e_{vf} - e_v$  is tuned to excite B to a final state where interconversion between the D and L chiral states can readily take place. This means that  $v_f$ , the final vibrational quantum number of B, can be either symmetric with respect to inversion  $B_{vf} = B_S$  or antisymmetric with respect to inversion,  $B_{vf} = B_A$ .

Let us choose the initial state of A–B to be symmetric. This means that

$$c_{D,L} = c_{L,D} \equiv C$$

The wave packet formed as a result of the action of this pulse is of the form

$$|\Psi_{vf}(\mathbf{R}, t)\rangle = 2\pi\epsilon_2(\omega_2) N(k) e^{-iE't + ik \cdot \mathbf{R}} C |B_{vf}\rangle \{ |A_D\rangle \langle B_{vf}| d_2 |B_L\rangle + |A_L\rangle \langle B_{vf}| d_2 |B_D\rangle \} \quad (29)$$

where  $E' = e_{vf} + k^2/(2\mu)$ . Due to the presence of the  $|A_D\rangle$  and  $|A_L\rangle$  state vectors, the two terms above do not interfere. In their absence,  $|\Psi_{vf}\rangle$  would have become symmetric with respect to inversion of fragment B.

To see this more clearly, we calculate the probability-density of B by squaring the above expression and integrating over  $\mathbf{R}$  and the A internal variables. We find, using the orthogonality of  $|A_D\rangle$  and  $|A_L\rangle$ , that

$$\rho_{vf}(\mathbf{r}) = |2\pi\epsilon_2(\omega_2) N(k) C B_{vf}(\mathbf{r})|^2 \{ |B_{vf}| d_2 |B_L\rangle|^2 + |B_{vf}| d_2 |B_D\rangle|^2 \} \quad (30)$$

Since each of the  $|\langle B_{vf}| d_2 |B_L\rangle|^2$  and  $|\langle B_{vf}| d_2 |B_D\rangle|^2$  terms allows it, transitions to both the symmetric and antisymmetric  $|B_{vf}\rangle$  states can be observed, exactly as in the collapsed wave function. It is interesting to note that it is the remote presence of the chiral fragment A that guarantees that the local properties of its entangled partner B prevail. This is despite the fact that these properties are different from those of the original A–B wave function.

#### V. Conclusion

We have shown on the basis of the properties of the solutions of the Schrödinger equation, that no information can be transferred between observers of two fragments resulting from the photodissociation of a polyatomic molecule, as a mere result of the performance of measurements on either fragment. We have shown this to be the case even if we consider the possibility that this information can somehow be transferred at speeds smaller than the speed of light.

We have also shown that when dissociation with sufficiently broad-band pulses is performed, the measurement of the momentum of one fragment is not enough to collapse the wave function of the other fragment. As a result, one can observe coherences between many internal states of fragments resulting from coherences induced in their parent molecule.

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