Can Covalently Bonded Molecules Pass Through Each Other by Quantum Tunnelling?

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1. Motivation and Answer

You may suspect that the answer to the question posed in the title is “no”, since otherwise you would have heard of such a thing. That is indeed the answer, but why? It is not so self evident as it may at first appear.

The motivation for considering this question (amongst possibly many others) is that it would provide a potential means of overcoming geometrical frustration in protein folding. If a strand of protein were to fold the wrong way and find itself on the ‘wrong’ side of some group further down the molecule, it could tunnel its way through to the correct side (driven, one supposes, by an energy gradient). However, this cannot happen, as we demonstrate here.

2. The Lazy Response

Ask any chemist this question and (s)he will reply that tunnelling probability reduces exponentially with mass. Hence, whilst an electron can tunnel readily, the far greater mass of a molecule (or, indeed, just a single nucleus) effectively eliminates the possibility of tunnelling.

It turns out that this answer is basically correct, but one has to work a little harder to make it fully convincing. The reason is that there is an obvious objection to this qualitative argument. Physically one could claim that it is only necessary for the electrons comprising the covalent bond to tunnel. If so, it is only the electron mass which enters the tunnelling expression, not the atomic or molecular masses.

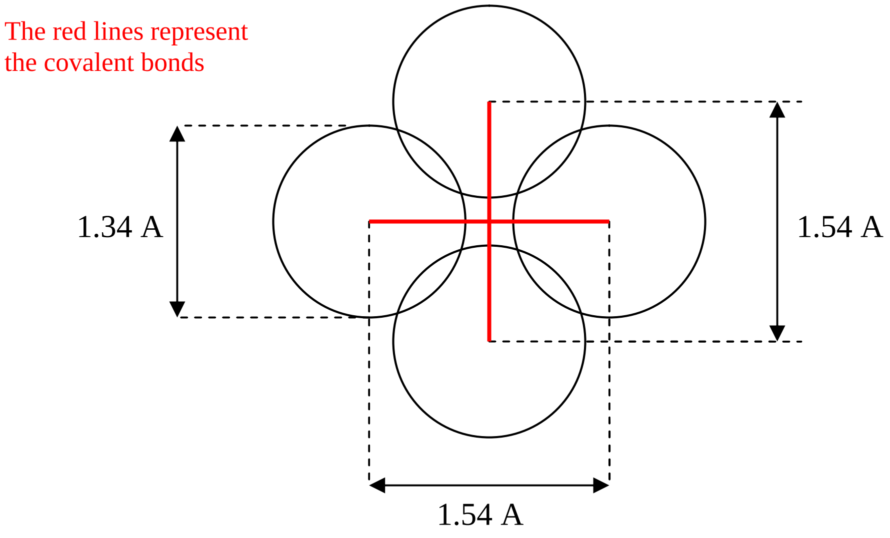
Consider a molecule consisting of two groups, A and B, which are joined by a single covalent bond. Similarly a second molecule consists of C and D bound by a single covalent bond. Provided that the geometry of the molecules A-B and C-D are compatible, the only obstacles to their passing through each other at the position of these single bonds are the bonds themselves. It is thus only necessary for the electron clouds which comprise the bonds to be able to pass through each other to accomplish the task for the molecules as a whole. However, this will be true only so long as the size of the atoms and the length of the bonds does not cause the atoms to collide.

3. Is Pass-Through Geometrically Possible?

It is not clear that there is necessarily any unavoidable geometrical ‘jamming’, at least for suitably chosen molecules. Consider an alkane for example. Every carbon atom has four single bonds which are roughly tetrahedrally disposed. The C-C bond length is 1.54 Angstrom. The nominal diameter of a carbon atom is 1.34 Angstrom. Consequently if we imagine two covalent bonds attempting to pass through each other at right angles there is an apparent conflict, as illustrated below in Figure 1. The distance between the centres of unbonded carbon atoms is $1.54 / \sqrt{2} = 1.09$ Angstrom. This is smaller than the atomic size and hence the carbon atoms are in conflict and will apparently prevent molecular tunnelling.

However, this is too simplistic. For a start, the atoms are not hard spheres with a clearly defined diameter. A degree of overlap of electron clouds may be possible, depending upon the energies involved.

Figure 1: Apparent Geometrical Conflict Between Carbon Atoms



Perhaps more importantly the atoms will be severely distorted from their shape when isolated by the tetrahedrally disposed sigma bonds. Each carbon atom has four electrons occupying sp^3 hybrid orbitals. The greatest density of the electron cloud which comprises each sigma bond lies between the nuclei which are thus bonded. Consequently, the above picture is very misleading.

The three other bonds on each carbon atom will drag a large proportion of the associated electron cloud away from the region of the bond in question in Figure 1. This will significantly shrink the effective size of the atom. Note that the bonds shown in Figure 1 do not count in this respect, since these are the electrons whose tunnelling we are to investigate (and hence overlap of these electron clouds is to be addressed directly). The only electrons not involved in bonding are the two 1S inner shell electrons. But the size of this orbital will be very small indeed, perhaps one-sixth of a Bohr radius (due to the carbon nucleus having charge 6e), i.e., an inner 'core' diameter of ~0.2 Angstrom.

Whilst these observations do not prove that molecular tunnelling is geometrically possible, they illustrate that geometrical frustration cannot be simply asserted. Hence geometry alone does not provide an impossibility argument against molecular tunnelling.

For the purposes of this note we shall assume tunnelling is *not* prevented by geometry. What remains is to investigate whether the quantum tunnelling itself is possible.

4. Archetypal Tunnelling: The1D Potential Barrier

The archetypal example of quantum tunnelling is to consider a free particle with kinetic energy E which hits a 'square' potential barrier of height V and width a. If $V > E$ then in classical physics the particle could never penetrate the barrier. In quantum mechanics, however, it may do so. It is an elementary problem, solved in standard texts, to show that the probability that the particle penetrates the barrier is,

$$\frac{16\alpha}{(1+\alpha)^2}\exp\{-2\kappa a\} \tag{1}$$

where, $$\alpha = \frac{V-E}{E} \tag{2}$$

and, $$\kappa = \frac{\sqrt{2m(V-E)}}{\hbar} \tag{3}$$

Equ.(1) holds only in the limit $\kappa a >> 1$, for which the probability of barrier penetration is small. For a barrier which is not a ‘square’ potential, we can estimate the barrier penetration probability by using an average decay rate, κ, given by,

$$\kappa a = \int_0^a \frac{\sqrt{2m(V(x)-E)}}{\hbar} dx \tag{4}$$

5. Implications for Electrons and Atoms

In (3) or (4), the mass, *m*, is the mass of the projectile which is, or is not, tunnelling through the barrier. Let us suppose for a moment that this is an electron, and hence of mass 9.1 x 10^{-31} kg. Suppose the barrier height is ~1 eV greater than the particle’s kinetic energy and suppose the barrier width is ~1 Angstrom. In terms of order of magnitude we can approximate the tunnelling probability by simply $\exp\{-2\kappa a\}$. This evaluates to $\sim e^{-1}$, i.e., a very large probability.

Now what if we assume the same potential barrier and impact kinetic energy, but take the effective particle mass to be (say) the mass of a pair of carbon atoms, i.e., m ~ 4 x 10^{-26} kg. We now get a tunnelling probability of order $e^{-215} \sim 10^{-93}$. Clearly tunnelling just will not happen with this effective mass. This, of course, is what chemists mean when they talk about the “exponential mass dependence of quantum tunnelling”.

Just how small would $V-E$ need to be before tunnelling might feasibly occur if the effective mass were that of two carbon atoms? With $V-E=0.1$ eV we get a tunnelling probability of ~10^{-30}, still too small to be significant, and with $V-E=0.01$ eV we get a tunnelling probability of ~10^{-9}. If coupled with a large frequency of attempts at penetration, this might just be significant. With $V-E=1$ meV we get a tunnelling probability of ~10^{-3}, which is now quite clearly significant.

Thus, if the effective mass is indeed that of the carbon atoms then tunnelling will not occur if the potential barrier exceeds the kinetic energy by more than a few meV.

On the other hand, if the effective mass is that of the electrons then a potential barrier which exceeds the kinetic energy by the order of eV can easily be penetrated.

Which is the relevant case? This is the question which is not so trivial to answer.

6. The Born-Oppenheimer Approximation

Put the question of two interacting molecules aside for a moment. Consider instead how we calculate a molecular orbital between two atoms. Let’s simplify the problem to that of just two electrons, which comprise the covalent bond in question, plus the two nuclei which are thus bound. The coordinates of these four particles are written $\bar{r}_1, \bar{r}_2, \bar{r}_A, \bar{r}_B$ and the Schrodinger equation is, (5)

$$\left[\frac{\hbar^2}{2M_A}\nabla_A^2 + \frac{\hbar^2}{2M_B}\nabla_B^2 + \frac{\hbar^2}{2m}\nabla_1^2 + \frac{\hbar^2}{2m}\nabla_2^2 + V(\bar{r}_1, \bar{r}_2, \bar{r}_A, \bar{r}_B)\right]\psi(\bar{r}_1, \bar{r}_2, \bar{r}_A, \bar{r}_B) = E\psi(\bar{r}_1, \bar{r}_2, \bar{r}_A, \bar{r}_B)$$

where V accounts for all the pair-wise Coulomb interactions between the two electrons and the two nuclei. (5) is already an approximation since we have ignored the other electrons around the two atoms, and this implies that the potential function V in (5) must be some approximate expression accounting for the shielding of the nuclei by the other electrons. The Born-Oppenheimer approximation appeals to the kinetic energy of the nuclei being small compared with that of the electrons. The first two operators on the LHS of (5) can thus be dropped to yield an equation for the electrons only,

$$\left[\frac{\hbar^2}{2m}\nabla_1^2 + \frac{\hbar^2}{2m}\nabla_2^2 + V(\bar{r}_1,\bar{r}_2,\bar{r}_A)\right]\psi_e(\bar{r}_1,\bar{r}_2,\bar{r}_A) = E_e(\bar{r}_A)\psi_e(\bar{r}_1,\bar{r}_2,\bar{r}_A) \tag{6}$$

The coordinate of nucleus B has been dropped since this (or, better, the centre of mass) can be taken as the origin. The (relative) position of nucleus A is essential in (6) since the proximity of the nuclei is crucial to the interaction energy between the electrons. However, in (6) $\bar{r}_A$ appears as a constant parameter (which is yet to be found). Consequently, the energy of the pair of electrons, E_e, in (6) is dependent upon $\bar{r}_A$. The eigenfunctions $\psi_e(\bar{r}_1,\bar{r}_2,\bar{r}_A)$ are therefore also dependent upon $\bar{r}_A$.

Implicit in (6) is that the ‘internal’ wavefunction of the (two atom) molecule can be written,

$$\psi = \psi_e(\bar{r}_1,\bar{r}_2,\bar{r}_A)\psi_n(\bar{r}_A) \tag{7}$$

We refer to (7) as the ‘internal’ wavefunction because the molecule as a whole is assumed stationary. Hence the wavefunction corresponding to its centre-of-mass coordinate, $\bar{R}$, is not explicitly shown. If it were, (7) would have an extra factor $\Phi(\bar{R})$. Substituting (7) into (5) and using (6) gives,

$$\left[\frac{\hbar^2}{2\mu_A}\nabla_A^2 + E_e(\bar{r}_A)\right]\psi_e(\bar{r}_1,\bar{r}_2,\bar{r}_A)\psi_n(\bar{r}_A) = E\psi_e(\bar{r}_1,\bar{r}_2,\bar{r}_A)\psi_n(\bar{r}_A) \tag{8}$$

where the reduced mass is $\mu_A = \dfrac{M_A M_B}{M_A + M_B}$. The next step in the Born-Oppenheimer approximation is to assume that the dependence of the electrons’ wavefunction, $\psi_e(\bar{r}_1,\bar{r}_2,\bar{r}_A)$, on $\bar{r}_A$ is modest so that we can approximate,

$$\nabla_A^2\left[\psi_e(\bar{r}_1,\bar{r}_2,\bar{r}_A)\psi_n(\bar{r}_A)\right] \approx \psi_e(\bar{r}_1,\bar{r}_2,\bar{r}_A)\nabla_A^2\psi_n(\bar{r}_A) \tag{9}$$

Physically this depends upon the amplitude of the nuclear motions being small compared with their equilibrium distance. This will be true unless very high vibrational modes, or rotational modes, are excited. Consequently the electron wavefunction factors out of (8) to leave a wavefunction for the nuclei alone,

$$\left[\frac{\hbar^2}{2\mu_A}\nabla_A^2 + E_e(\bar{r}_A)\right]\psi_n(\bar{r}_A) = E\psi_n(\bar{r}_A) \tag{10}$$

Note that since we assuming that the electrons are in a bound state, the total electron energy, E_e in (6) is a negative quantity. Hence the effect of this term in (10) is to act as an attractive potential which in turn binds the two nuclei – thus creating the chemical bond. It follows that the total energy, E, is also negative (or the atoms would not be bound). Note that it is clear from (5) that E is the total ‘internal’ energy of all four particles comprising the molecule, the two electrons and the two nuclei, since (5) includes all the internal potential energies and all four kinetic energy terms. The binding energy, i.e., the energy required to pull the two atoms apart to leave a pair of neutral atoms, is $\left|E - \langle E_e \rangle\right|$, where $\left\langle E_e \right\rangle$ is the expectation value of $E_e(\bar{r}_A)$ for the eigen-state, $\psi_n(\bar{r}_A)$, in question.

7. The Interaction of Two Molecules

Now we come to the nub of the matter. Consider two molecules: the first A-B consisting of two groups, A and B, joined by a single covalent bond, and the second C-D with a similar single covalent bond. Assuming no geometrical frustration, can these two covalent bonds pass through each other? The bonds consist, of course, of dispersed clouds of electrons. The only thing to prevent their passing, ghost-like, through each other is their mutual electrostatic repulsion, i.e., the energy barrier between the two electron clouds.

The two electrons comprising the bond A-B are assigned coordinates $\bar{r}_1, \bar{r}_2$, whereas those on the other molecule, comprising the bond C-D, are at $\bar{r}_3, \bar{r}_4$. The distance apart of the nuclei on either side of the A-B bond is $\bar{r}_A$, and the distance apart of the nuclei on either side of the C-D bond is $\bar{r}_C$. Finally, the distance apart of the centres of mass of the two molecules is $\bar{R}$. Hence our eight particles (four electrons plus four nuclei) are described by seven vector coordinates (the centre of mass of the two molecules taken as a whole being ignored, i.e., stationary). The Schrodinger equation for this eight-particle system is thus,

$$\begin{bmatrix} \dfrac{\hbar^2}{2\mu_A}\nabla_A^2 + \dfrac{\hbar^2}{2\mu_C}\nabla_C^2 + \dfrac{\hbar^2}{2\mu}\nabla_R^2 + \dfrac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \nabla_4^2\right) + \\ V_{AB}(\bar{r}_1, \bar{r}_2, \bar{r}_A) + V_{CD}(\bar{r}_3, \bar{r}_4, \bar{r}_C) + V_{\text{int}}(\bar{r}_1, \bar{r}_{2,}, \bar{r}_3, \bar{r}_4, \bar{r}_A, \bar{r}_C, \bar{R}) \end{bmatrix} \psi = E\psi \qquad (11)$$

The wavefunction in (11) depends upon all coordinates, $\psi\left(\bar{r}_1, \bar{r}_{2,}, \bar{r}_3, \bar{r}_4, \bar{r}_A, \bar{r}_C, \bar{R}\right)$. The terms μ_A and μ_C are the reduced masses of the nuclei on either side of the A-B bond, and on either side of the C-D bond, respectively. Similarly, μ is the reduced mass of the two molecules.

The term V_{AB} is the intra-molecular potential energy of molecule A-B. (To be more exact, it is that part of the intra-molecular energy which relates to the pair of bonding electrons plus the two bound nuclei. The rest of the groups A and B are not counted in this energy inventory). Similarly, V_{CD} is the intra-molecular potential energy of molecule C-D. The last term on the LHS of (11), V_{int}, is the interaction potential between the two molecules – assuming that only the four electrons and four nuclei involved in the two bonds contribute.

The energy, *E*, in (11) is the sum of all the potential energies due to all pair-wise interactions between the eight involved particles, plus the eight kinetic energy terms.

Let us now suppose that the wavefunction in (11) can be considered as the product of the wavefunctions for each molecule times a function which relates to their relative bulk motion in terms of coordinate $\bar{R}$, thus,

$$\psi\left(\bar{r}_1, \bar{r}_{2,}, \bar{r}_3, \bar{r}_4, \bar{r}_A, \bar{r}_C, \bar{R}\right) = \psi_{AB}\left(\bar{r}_1, \bar{r}_{2,}, \bar{r}_A\right)\psi_{CD}\left(\bar{r}_3, \bar{r}_4, \bar{r}_C\right)\Phi\left(\bar{R}\right) \qquad (12)$$

Equ.(11) therefore becomes,

$$\left[\frac{\hbar^2}{2\mu}\nabla_R^2 + V_{\text{int}}\left(\bar{r}_1, \bar{r}_{2,}, \bar{r}_3, \bar{r}_4, \bar{r}_A, \bar{r}_C, \bar{R}\right)\right]\psi = \left(E - E_{AB} - E_{CD}\right)\psi \qquad (13)$$

Here, E_{AB} is the total energy of the four particles involved in the A-B bond, and is therefore negative, as is E_{CD}. They are the values of E in Equ.(10) and hence are the energies required both to break the molecular bond and also to ionise the atoms and release the electrons.

Note that the molecular wavefunctions ψ_{AB} and ψ_{CD} factor out of Equ.(13) to leave an equation in $\Phi\left(\bar{R}\right)$ alone. However, there is a problem: the interaction potential in (13) still contains dependence upon the coordinates $\bar{r}_1, \bar{r}_{2,}, \bar{r}_3, \bar{r}_4, \bar{r}_A, \bar{r}_C$. What has happened here is that we have effectively assumed that the molecular wavefunctions, ψ_{AB} and ψ_{CD}, are unchanged by the inter-molecular interaction, V_{int}. This is equivalent to employing first order perturbation theory, in which case the effective interaction can be replaced by its expectation value for the molecular states in question. Hence we must make the replacement,

$$V_{\text{int}}\left(\bar{r}_1, \bar{r}_{2,}, \bar{r}_3, \bar{r}_4, \bar{r}_A, \bar{r}_C, \bar{R}\right) \to \left\langle V_{\text{int}} \right\rangle \equiv \left\langle \psi_{AB}, \psi_{CD} \middle| V_{\text{int}} \middle| \psi_{AB}, \psi_{CD} \right\rangle \qquad (14)$$

Explicitly this ‘average’ interaction energy is, (15)

$$\left\langle V_{\text{int}} \right\rangle = \int V_{\text{int}}\left(\bar{r}_1, \bar{r}_{2,}, \bar{r}_3, \bar{r}_4, \bar{r}_A, \bar{r}_C, \bar{R}\right) \left|\psi_{AB}\left(\bar{r}_1, \bar{r}_2, \bar{r}_A\right)\right|^2 \left|\psi_{CD}\left(\bar{r}_3, \bar{r}_4, \bar{r}_B\right)\right|^2 d^3r_1 d^3r_2 d^3r_3 {}^3r_4 d^3r_A d^3r_C$$

so that $\left\langle V_{\text{int}} \right\rangle \equiv \tilde{V}_{\text{int}}\left(\bar{R}\right)$ retains a dependence upon the separation of the two molecules, $\bar{R}$. So finally (13) becomes simply,

$$\left[\frac{\hbar^2}{2\mu}\nabla_R^2 + \tilde{V}_{\text{int}}\left(\bar{R}\right)\right]\Phi\left(\bar{R}\right) = \tilde{E}\Phi\left(\bar{R}\right) \qquad (16)$$

where, $\tilde{E} = E - E_{AB} - E_{CD}$

The energy $\tilde{E}$ is the total energy, potential plus kinetic, of the eight involved particles *minus* the total energy internal to each molecule. It is thus the total potential plus kinetic energy associated with the pair of molecules if they are regarded as structureless point particles. If the molecules could bind together to form a composite molecule then $\tilde{E}$ could be negative. However, we are assuming that no bound state of the two molecules is relevant here. Rather, the two molecules collide with some significant kinetic energy and the total energy term $\tilde{E}$ is positive. Since the interaction is negligible at large distances, the energy $\tilde{E}$ can be equated with the total incoming kinetic energy of the pair of molecules treated as point masses.

The molecules are envisaged as attempting to pass through each other, the nuclei not coming into contact but the molecules crossing over at roughly the middle of their covalent bonds. It is therefore the two electron clouds comprising these bonds which come into the most intimate contact. The interaction energy, (15), will therefore be dominated by the electrostatic repulsion of these electron clouds, and hence will be a positive energy, $\tilde{V}_{\text{int}} > 0$.

Equ.(16) is therefore of the form where quantum tunnelling might be considered, i.e., it describes an incoming particle with positive energy hitting a positive potential energy barrier. If $\tilde{E} > \tilde{V}_{\text{int}}$ then it is assured that the probability of penetration will be high (in fact more probable than not). However, the situation, as we shall see below, is that $\tilde{E} << \tilde{V}_{\text{int}}$ and the probability of tunnelling is of order $\exp\{-2\kappa a\}$ where,

$$\kappa a = \int_{-a/2}^{+a/2} \frac{\sqrt{2\mu\left(\tilde{V}_{\text{int}}(R) - \tilde{E}\right)}}{\hbar} dR \tag{17}$$

(see §4). The function $\tilde{V}_{\text{int}}(\overline{R})$, including its effective 'width', *a*, can in principle be calculated from (15).

The important thing to note about (17) is that it contains the reduced nuclear mass, not the electron mass. This is a consequence of the fact that the tunnelling equation is (16) and this is the equation which defines the bulk relative motion of the two molecules. This is the key result. It is now fairly obvious from the general considerations of §5 that tunnelling of the two molecules is not credible. For completeness the argment is laid out below.

8. Implications for Molecular Tunnelling

It would be quite feasible to estimate the interaction potential, $\tilde{V}_{\text{int}}$, by assuming it to be dominated by the electron-electron Coulomb terms between the molecules, thus,

$$V_{\text{int}}\left(\bar{r}_1, \bar{r}_{2,}, \bar{r}_3, \bar{r}_4, \bar{r}_A, \bar{r}_C, \overline{R}\right) \approx \frac{e^2}{4\pi\varepsilon_0|\bar{r}_1 - \bar{r}_3|} + \frac{e^2}{4\pi\varepsilon_0|\bar{r}_1 - \bar{r}_4|} + \frac{e^2}{4\pi\varepsilon_0|\bar{r}_2 - \bar{r}_3|} + \frac{e^2}{4\pi\varepsilon_0|\bar{r}_2 - \bar{r}_4|}$$

With the aid of some approximate solution for the sp^3 molecular orbitals, the interaction energy $\tilde{V}_{\text{int}}$ could then be found by direct evaluation of the integrals in (15). However, it really is not worth taking such trouble, as will become clear from the following rough order-of-magnitude estimate.

Let us idealise the sp^3 molecular orbitals as being significant only between the bonded nuclei. More specifically we shall approximate the electron density, $|\psi_{AB,e}|^2$, to be uniform within a sphere centred on the mid-point of the bond and of diameter *a* but zero outside this sphere. Note that this diameter also acts as an effective 'width' of the potential $\tilde{V}_{\text{int}}$ since the interaction energy will fall off as the overlap between the two electron clouds diminishes. It is elementary to determine the electrical potential due to a uniform sphere of charge. Since the total charge per cloud is 2*e* (because each bond consists of two electrons), this is,

$$\text{For } r \le a/2: \quad \phi = \left(\frac{3}{2} - 2\frac{r^2}{a^2}\right)\frac{e}{\pi\varepsilon_0 a}; \qquad \text{For } r \ge a/2: \quad \phi = \frac{e}{2\pi\varepsilon_0 r} \tag{18}$$

This solution has continuous ϕ and continuous electric field $-\frac{\partial\phi}{\partial r}$ at $r = \frac{a}{2}$, as it must. The interaction energy between the two electron clouds is greatest when the two spheres are exactly superimposed (i.e., when $R = 0$). So we have,

$$\tilde{V}_{\text{int}}^{\max} = \int_0^{a/2} \phi(r) \cdot \rho \cdot 4\pi r^2 dr \tag{19}$$

and $\rho = \dfrac{2e}{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3} = \dfrac{48e}{4\pi a^3}$, so that (19) becomes,

$$\tilde{V}_{\text{int}}^{\text{max}} = \frac{48e}{a^3}\int_0^{a/2}\left(\frac{3}{2} - 2\frac{r^2}{a^2}\right)\frac{e}{\pi\varepsilon_0 a}\cdot r^2 dr = \frac{12e^2}{5\pi\varepsilon_0 a} \qquad (20)$$

Rather than evaluating $\tilde{V}_{\text{int}}$ as a function of the distance between the molecules, *R*, and then calculating the integral in (17), we merely approximate κa as the peak value of κ derived from (20) times the diameter of the spheres of charge, *a*.

If we take *a* to be the bond length (1.54 Angstrom), which seems most appropriate, we get $\tilde{V}_{\text{int}}^{\text{max}} = 90$ eV. This is a very large energy by the standards of atomic, or molecular, electron states. Body temperature (310 K) corresponds to kT of 0.027 eV, which will therefore be the typical magnitude of the kinetic energies of the molecules per degree of freedom. Even accounting for several involved degrees of freedom, and some reasonable number of standard deviations from the mean of the Maxwell distribution, it is clear that the effective $\tilde{E}$ will be less than 1 eV.

Consequently the value of κa is of order $\kappa a \sim \dfrac{a\sqrt{2\mu\tilde{V}_{\text{int}}^{\text{max}}}}{\hbar} \sim 550$. Here we have taken the reduced mass of the two molecules as one-quarter the mass of a single carbon atom (1/4 x 2 x 10^{-26} kg). Since the carbon atoms on either side of the two bonds will be required to drag the rest of the molecular groups A, B, C and D along with them, this may be rather an under-estimate. The tunnelling probability is therefore of the order $\exp\{-2\kappa a\} = \exp\{-1100\}$ which is effectively zero.

If we choose an effective charge diameter, *a*, which is only half as big, then κa reduces by a factor $1/\sqrt{2}$ and the tunnelling probability becomes $\exp\{-780\}$, still effectively zero.

It is clear that any reasonable temperature consistent with the molecules not being dissociated (and, indeed, the atoms not being ionized as well) cannot raise the effective $\tilde{E}$ to anywhere near $\tilde{V}_{\text{int}}^{\text{max}}$.

Whilst covalent bonds between atoms other than carbon atoms will differ in detail, it is clear that any such differences cannot challenge the fact that the potential energy of superimposed electron clouds of the two covalent bonds will be orders of magnitude larger than available thermal energies.

We conclude that the quantum tunnelling of two covalently bonded molecules through each other is not possible.