Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Distance and orientation dependence of photoinduced electron transfer through twisted, bent and helical bridges: a Karplus relation for charge transfer interaction

René M. Williams

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Dedicated to Tibbe Antoon Williams, born February 8, 2010.

Molecular Photonics Group, Van 't Hoff Institute for Molecular Sciences,

Faculty of Science, Universiteit van Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands, phone +31 (0)20 525 5477, fax: +31 (0)20 525 6456, R.M.williams@uva.nl

Supporting information

Content:

1
Text of Igor 6 procedure file to visualize and make fits with equation (B). See also .ipf file.

2
Derivation of equation (B).
See also Appendix of manuscript.

3
Examples of other mathematically possible fits of figure 10, using equation (B), that have ‘less physical meaning”.

4
A *Wolfram* Mathematica Player file with an "interactive" adaptable form of equation (B), showing the effects of four parameters, also available in .nbp form.
Wolfram Mathematica Player can be downloaded here:

http://www.wolfram.com/products/player/

1

An Igor 6 procedure file is given separately as SI, as and .ipf file.
Below is the text of the Igor 6 procedure file that can be used to make fits and visualize equation (B):

```
#pragma rtglobals=2

Function betafactor3(FG_ParamWave, x) : FitFunc
	Wave FG_ParamWave
	Variable x

	//CurveFitDialog/
	//CurveFitDialog/ Independent Variables 1
	//CurveFitDialog/ x
	//CurveFitDialog/ Coefficients 6
	//CurveFitDialog/ FG_ParamWave[0] = a
	//CurveFitDialog/ FG_ParamWave[1] = b
	//CurveFitDialog/ FG_ParamWave[2] = k
	//CurveFitDialog/ FG_ParamWave[3] = betaa
	//CurveFitDialog/ FG_ParamWave[4] = Re
	//CurveFitDialog/ FG_ParamWave[5] = betaS

	Variable a = FG_ParamWave[0]
	Variable b = FG_ParamWave[1]
	Variable k = FG_ParamWave[2]
	Variable betaa = FG_ParamWave[3]
	Variable Re = FG_ParamWave[4]
	Variable betaS = FG_ParamWave[5]

	return (sin((a*pi*x+pi)/2)^2+cos(b*pi*x)^2)^2*k*exp(-betaa*Re*x)+k*exp(-
betaS*Re*x)
end
```

2

Here a derivation is given of equation (B).

As a starting point we focus on equation (A)

$$k_{cs} = k_0 \times e^{-\beta R_e} \qquad \text{(A)}$$

We can find its origins in Atkins' Physical Chemistry (8^{th} edition) page 897-898, from which we quote:

"The tunneling event responsible for electron transfer is similar to normal tunneling, except that in this case the electron tunnels from an electronic level of D, with wavefunction Ψ_D, to an electronic level of A, with wavefunction Ψ_A. The rate of an electronic transition from a level described by the wavefunction Ψ_D to a level described by the wavefunction Ψ_A is proportional to the square of the (overlap) integral ($\langle H_{DA} \rangle$)

$$\langle H_{DA} \rangle = \int \Psi_A \hat{\mathrm{H}}_{DA} \Psi_D d\tau$$

where H_{DA} (operator) is a Hamiltonian that describes the coupling of the electronic wavefunctions. It turns out that in cases where the coupling is weak we may write

$$\langle H_{DA} \rangle^2 = \langle H_{DA}^0 \rangle^2 e^{-\beta r}$$

where r is the edge-to-edge distance between D and A, β is a parameter that measures the sensitivity of the electronic coupling matrix element to distance, and $\langle H^0{}_{DA} \rangle^2$ is the value of the electronic coupling matrix element when D and A are in contact ($r = 0$). The exponential dependence on distance is essentially the same as the exponential decrease in transmission probability through a potential energy barrier.

From which we can obtain

$\ln k_{et} = -\beta r + \text{constant}$

which implies that a plot of ln k_{et} against r should be a straight line with slope $-\beta$."

This is identical to equation (A) in this manuscript using $k_{et} = k_{cs}$; $r = R_e$

We refer the reader to Atkins' original text for more details.

As noted in our reference 14 (*Principles of Molecular Photochemistry, An Introduction*, p. 442) this equation (A) assumes a spherical approach for D and A: it is set up for e.g. an s-orbital.

This implies that if we use an s-type wavefunction

$$\Psi_A = \Psi_D = R \times Y = (\frac{2}{a_0})^{3/2} e^{-r/a_0} \times (\frac{1}{4\pi})^{1/2}$$

for Ψ_A and Ψ_D, the integral gives us a radial dependent part in the form of equation (A). This model implies electron transfer from e.g. a singly occupied s-orbital to an empty s-orbital.

R is the radial part of the wavefunction, *Y* the angular part.

Filling in gives:

$$\langle H_{DA} \rangle^2 = (\int \Psi_A \hat{\mathrm{H}}_{DA} \Psi_D d\tau)^2 =$$

$$(\int ((\frac{2}{a_0})^{3/2} e^{-r/a_0} \times (\frac{1}{4\pi})^{1/2})_A \hat{\mathrm{H}}_{DA} ((\frac{2}{a_0})^{3/2} e^{-r/a_0} \times (\frac{1}{4\pi})^{1/2})_D d\tau)^2 = \langle H_{DA}^0 \rangle^2 e^{-\beta r} \qquad \text{(E)}$$

To obtain the angular part depending on ϕ and θ, we need to take a wavefunction with an non-constant angular component like a p-orbital, such as:

p_x

$$\Psi_A = \Psi_D = R \times Y = \frac{1}{2\sqrt{6}} (\frac{1}{a_0})^{3/2} (\frac{r}{a_0}) e^{-r/2a_0} \times (\frac{3}{4\pi})^{1/2} \sin\theta \cos\phi$$

p_y

$$\Psi_A = \Psi_D = R \times Y = \frac{1}{2\sqrt{6}} (\frac{1}{a_0})^{3/2} (\frac{r}{a_0}) e^{-r/2a_0} \times (\frac{3}{4\pi})^{1/2} \sin\theta \sin\phi$$

or p_z

$$\Psi_A = \Psi_D = R \times Y = \frac{1}{2\sqrt{6}} (\frac{1}{a_0})^{3/2} (\frac{r}{a_0}) e^{-r/2a_0} \times (\frac{3}{4\pi})^{1/2} \cos\theta$$

using Z = 1 for simplicity.

Keeping in mind that the rate of charge separation is a function of three variables: $k_{et}(r,\theta,\phi)$ we can now write the whole integral.
We take the transfer between two p_x orbitals (of e.g. a hydrogen atom and a proton; a half filled orbital and an empty one)

Equation (B) or our manuscript implies that:

$$\langle H_{DA}\rangle^2 = (\int \Psi_A \hat{\mathrm{H}}_{DA} \Psi_D d\tau)^2 =$$

$$(\int (\frac{1}{2\sqrt{6}}(\frac{1}{a_0})^{3/2}(\frac{r}{a_0})e^{-r/2a_0} \times (\frac{3}{4\pi})^{1/2} \sin\theta\cos\phi)_A \hat{\mathrm{H}}_{DA} (\frac{1}{2\sqrt{6}}(\frac{1}{a_0})^{3/2}(\frac{r}{a_0})e^{-r/2a_0} \times (\frac{3}{4\pi})^{1/2} \sin\theta\cos\phi)_D d\tau)^2 \qquad \text{(F)}$$

can be approximated by:

$$\langle H_{DA}\rangle^2 = (\langle H_{DA}^{\theta 0}\rangle \sin^2\phi + \langle H_{DA}^{\phi 0}\rangle \cos^2\theta)^2 \times e^{-\beta_a r} \qquad \text{(G)}$$

here, superscripts relating to θ *or* ϕ are introduced for the overlaps, and the β contains a subscript relating to angular dependant (*a)* value.
As the interaction of a p_x orbital with a p_z orbital will be independent of the twist angle, it must be that $\theta = \phi_T$ and $\phi = \phi_D$.

For clarity we repeat the important (empirical) equations from our manuscript:

$$V_D^t = V_i + V_a = V_i + V_D(\sin^2(\frac{\phi_D}{2}))$$

$$V_T^t = V_i + V_a = V_i + V_T(\cos^2\phi_T)$$

$$k_{cs}^t = k_{cs}^i + k_{cs}^a = k_0 \times e^{-\beta_i R_e} + (\sin^2(\frac{\phi_D}{2}) + \cos^2\phi_T)^2 \times k_0 \times e^{-\beta_a R_e} \qquad \text{(B)}$$

Note that $V = \langle H_{DA}\rangle$ and $r = R_e$

The approximation of the integral (F) will be part of forthcoming work.

It has to be noted that the approximation to (G) is "*a physical organic chemist's intuitive approach"* to a quantum chemical problem.
The integral (F) remains to be solved exact or numerical.

In order to solve the integral we need to correlate nine parameters:
r_D, r_A, r: respectively the distance to the nucleus of the electron of the donor, the distance to the nucleus of the acceptor to where the electron is transferred, the edge to edge distance between donor and acceptor (the internuclear distance minus the sum of the van der Waals radii of the two p-orbitals);
θ_D, ϕ_D, θ_A, ϕ_A, θ, ϕ: respectively the angular coordinates of the electron of the donor and of the hole on the acceptor and the twist and dihedral angles between donor and acceptor.

3

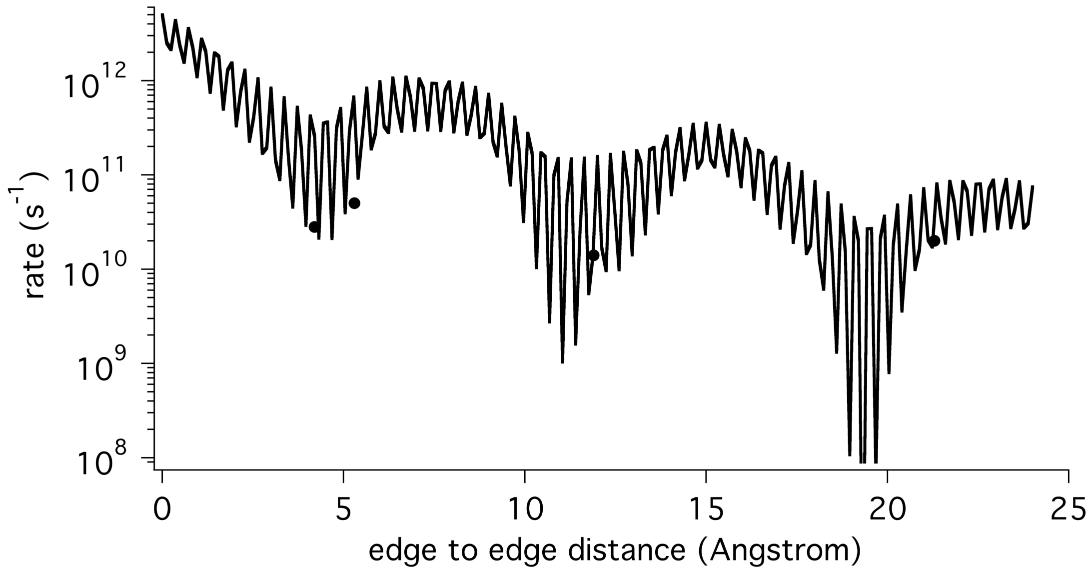

Figure S1.
Rates of charge separation as function of distance fitted with the "Karplus relation for CT interaction" (see text). The line in figure S1 was obtained with $a = 22$, b = 0.13, $k_0 = 1\times 10^{12}$, $\beta_a = 0.16$, $\beta_i = 0.9$, using

$$k_{cs}^{t}(R_e) = k_0 \times e^{-\beta_i R_e} + (\sin^2(\frac{a\pi R_e + \pi}{2}) + \cos^2(b\pi R_e))^2 \times k_0 \times e^{-\beta_a R_e}$$

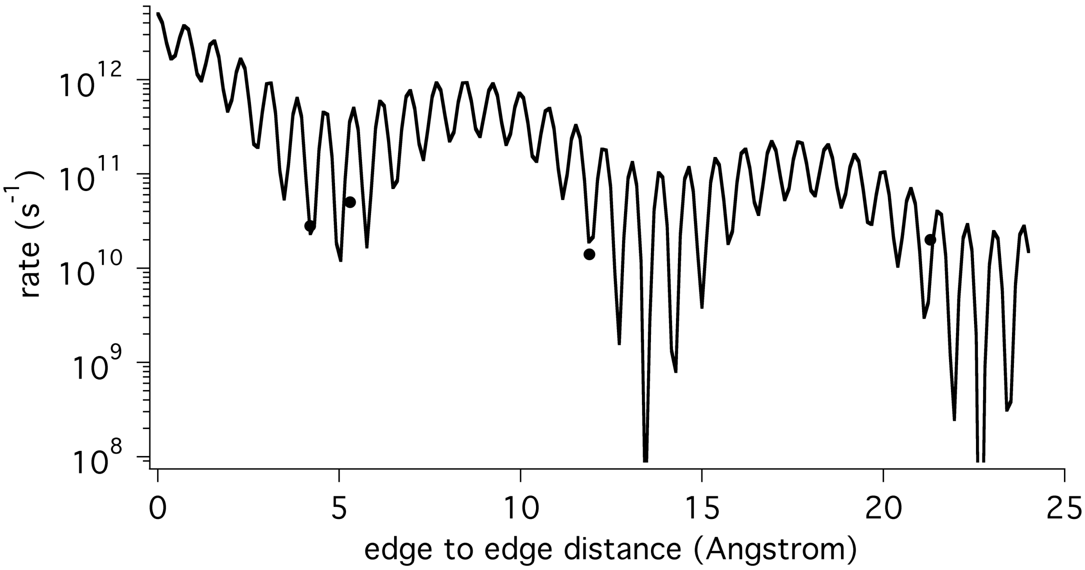

Figure S2.

Rates of charge separation as function of distance fitted with the "Karplus relation for CT interaction" (see text). The line in figure S2 was obtained with $a = 0.22$, $b = 1.3$, $k_0 = 1\times 10^{12}$, $\beta_a = 0.16$, $\beta_i = 0.9$, using

$$k^{t}_{cs}(R_e) = k_0 \times e^{-\beta_i R_e} + (\sin^2(\frac{a\pi R_e + \pi}{2}) + \cos^2(b\pi R_e))^2 \times k_0 \times e^{-\beta_a R_e}$$

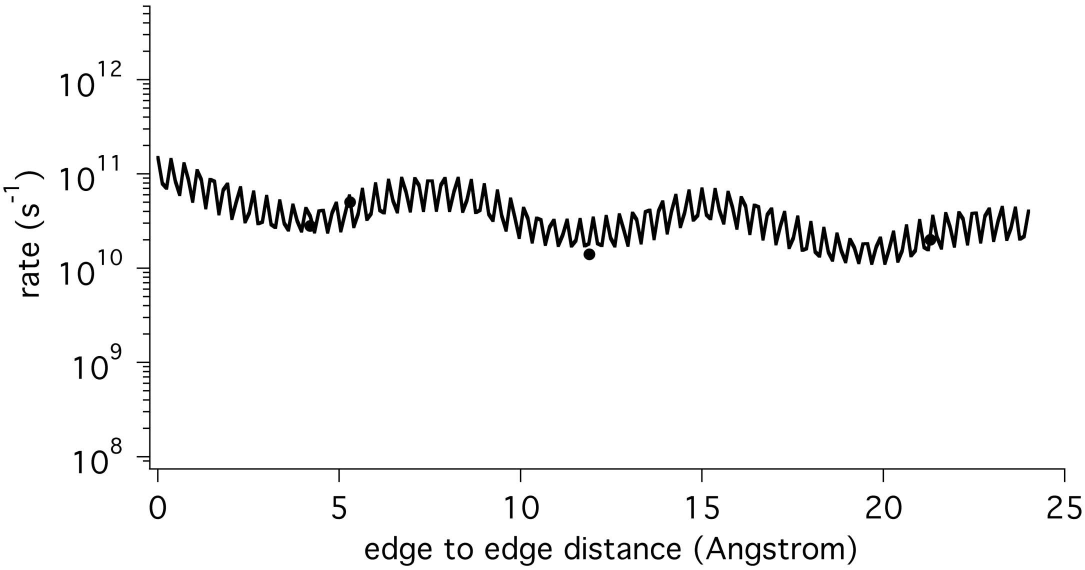

Figure S3.

Rates of charge separation as function of distance fitted with the "Karplus relation for CT interaction" (see text). The line in figure S3 was obtained with $a = 22$, b = 0.13, $k_0 = 3\times 10^{10}$, $\beta_a = 0.05$, $\beta_i = 0.05$, using

$$k^{t}_{cs}(R_e) = k_0 \times e^{-\beta_i R_e} + (\sin^2(\frac{a\pi R_e + \pi}{2}) + \cos^2(b\pi R_e))^2 \times k_0 \times e^{-\beta_a R_e}$$

SUPPORTING INFORMATION
belonging to :

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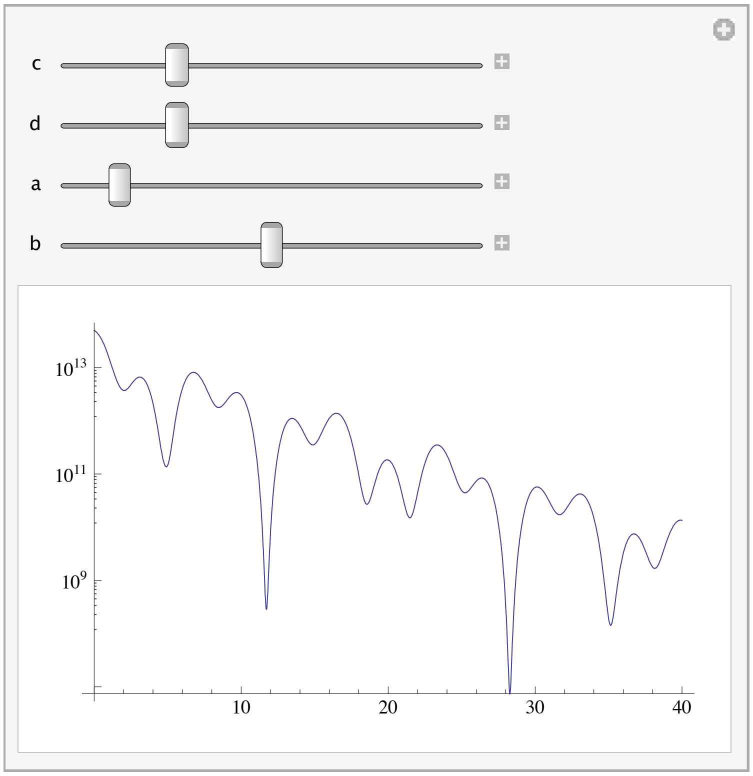
René M.Williams

Molecular Photonics Group, Van ' t Hoff Institute for Molecular Sciences,
Faculty of Science, Universiteit van Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam,
The Netherlands, phone + 31 (0) 205 255 477, fax : +31 (0) 205 256 456, R.M.williams@uva.nl

Below is an "interactive" adaptable form of equation (B), showing the effects of four parameters.

```
Manipulate[
 LogPlot[1 * 10^13 ((Sin[(0.25 * π * c * x + π) / 2])^2 + (Cos[0.3 * π * d * x])^2)^2 * (ⅇ^(-a * x)) +
   1 * 10^13 * (ⅇ^(-b * x)), {x, 0, 40}], {c, 0, 4}, {d, 0, 4}, {a, 0, 2}, {b, 0, 2}]
```



With regard to the derivation of equation (B)

It can be noted that the differential of equation (B) with respect to three parameters gives the function under the integral (see appendix) :

```
D[((Sin[(x)])^2 + (Cos[y])^2)^2 * (ⅇ^(-z)), x, y, z]
```

```
8 ⅇ^-z Cos[x] Cos[y] Sin[x] Sin[y]
```