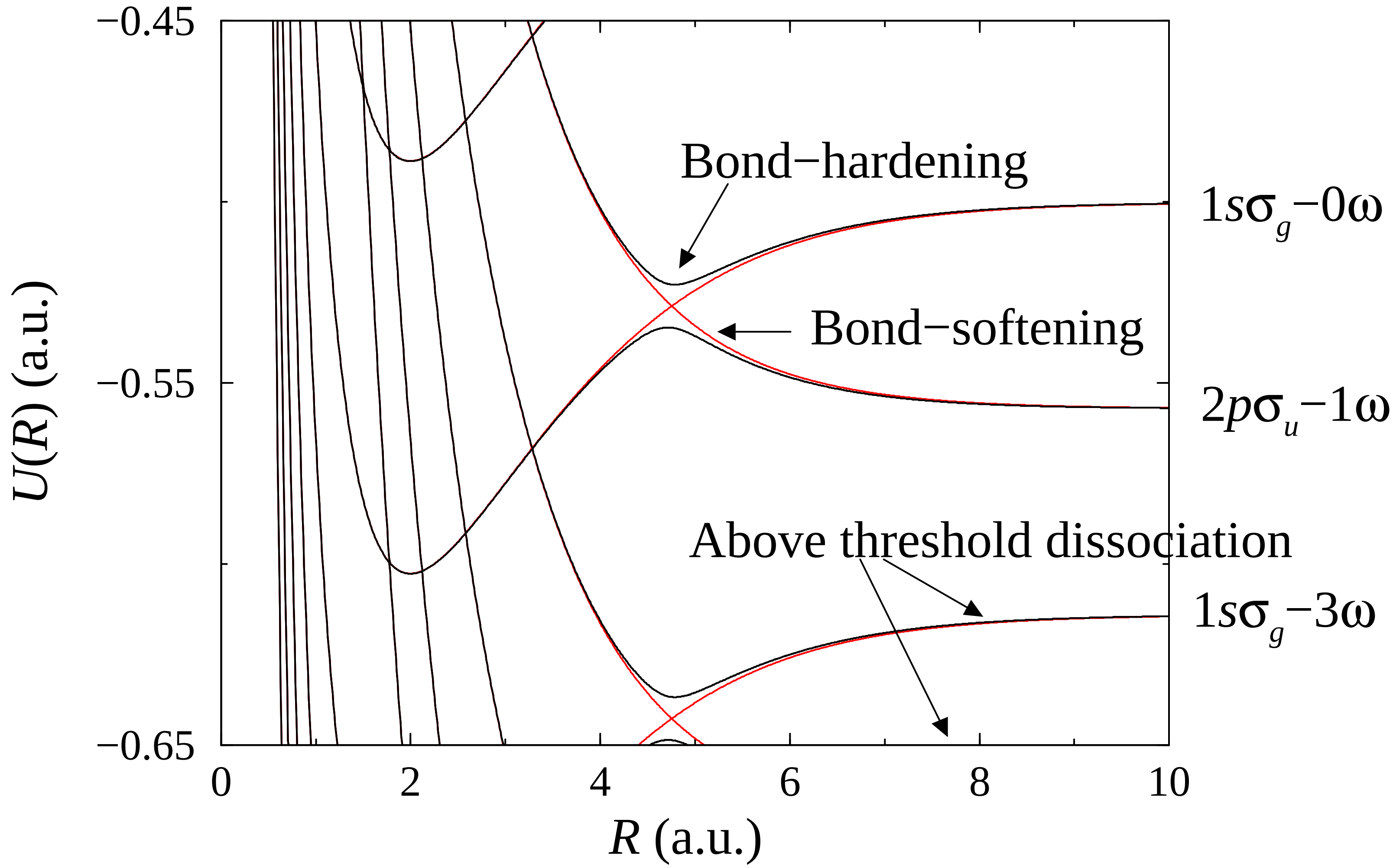
Re-examination of the Floquet Treatment of H_2^+

—— B.D. Esry ——

Very Useful Picture



Motivation and Goals

Motivation:

- To re-examine the many approximations made in the past
- Mistakes have been made (and published)

Goals:

- To give an explicit accounting of the coupling
- To show the limits of the usual two-channel approximation
- To show how to check whether a calculation is correct

Theory

D. Telnov and S.I. Chu, Phys. Rep. **390**, 1 (2004)

Want to solve

$$i\frac{\partial}{\partial t}\Psi(\mathbf{R},\mathbf{r},t) = H\Psi(\mathbf{R},\mathbf{r},t)$$

where

$$H = -\frac{1}{2\mu_{AB}}\frac{\partial^2}{\partial R^2} + H_{\mathrm{el}} + W(t)$$
$$W(t) = -\mathbf{E}\cdot\mathbf{d}\cos\omega t$$

and

$$\mathbf{d} = \frac{Z_B m_A - Z_A m_B}{m_{AB}}\mathbf{R} - \frac{m_{AB}+Z_{AB}}{m_{AB}+1}\mathbf{r}$$

Theory

Floquet Theorem says

$$\Psi(\mathbf{R}, \mathbf{r}, t) = e^{-i\varepsilon t}\psi(\mathbf{R}, \mathbf{r}, t)$$

with

$$\psi(\mathbf{R}, \mathbf{r}, t) = \psi(\mathbf{R}, \mathbf{r}, t + T)$$

giving

$$\left(H - i\frac{\partial}{\partial t}\right)\psi = \varepsilon\psi.$$

Can solve adiabatically (Born-Oppenheimer)

$$H_{\mathrm{ad}}\Phi_\nu(R; \Omega) = U_\nu(R)\Phi_\nu(R; \Omega)$$

where $\Omega = (\hat{R}, \mathbf{r}, t)$ and

$$H_{\mathrm{ad}} = H_{\mathrm{el}} + W(t) - i\frac{\partial}{\partial t}$$

Theory

Adiabatic states are complete with the definition

$$\langle \Phi_\lambda | \Phi_\nu \rangle = \int d\Omega \; \Phi_\lambda^* \Phi_\nu$$
$$= \frac{1}{T} \int_0^T dt \int d\hat{R} \int d^3 r \; \Phi_\lambda^* \Phi_\nu .$$

ψ periodic implies Φ periodic, so can use Fourier series

$$\Phi_\nu(R; \Omega) = \sum_{n=-\infty}^{\infty} \phi_{\nu n}(R; \hat{R}, \mathbf{r}) e^{-in\omega t}$$

giving

$$\big(H_{\mathrm{el}} - n'\omega\big)\, \phi_{\nu n'} + \sum_n \langle n' | W | n \rangle \phi_{\nu n} = U_\nu \phi_{\nu n'}$$

$$\langle n' | H_1 | n \rangle = \frac{1}{T} \int_0^T e^{i(n'-n)\omega t} W(t) dt = -\frac{1}{2} \mathbf{E} \cdot \mathbf{d} (\delta_{n',n+1} + \delta_{n',n-1})$$

Theory

We need to solve

$$(H_{\rm el} - n\omega)\,\phi_{\nu n} - \frac{1}{2}\mathbf{E}\cdot\mathbf{d}\,(\phi_{\nu n-1} + \phi_{\nu n+1}) = U_\nu \phi_{\nu n}$$

Theory

Neglecting nuclear rotation, can expand ϕ on field-free electronic states χ

$$\phi_{\nu n}(R,\theta;\mathbf{r}) = \sum_{\alpha\Lambda} a_{\nu n,\alpha\Lambda}(R,\theta)\chi_{\alpha\Lambda}(R;\mathbf{r}).$$

Writing

$$\mathbf{E}\cdot\mathbf{d} = d_{\parallel}E\cos\theta + d_{\perp}E\sin\theta$$

gives

$$\left(U^0_{\alpha\Lambda} - n\omega\right) a_{\nu n,\alpha\Lambda} - \frac{1}{2}\sum_{\alpha'\Lambda'}\langle\alpha\Lambda|\mathbf{E}\cdot\mathbf{d}|\alpha'\Lambda'\rangle \left(a_{\nu n-1,\alpha'\Lambda'} + a_{\nu n+1,\alpha'\Lambda'}\right) = U_\nu(R,\theta)a_{\nu n,\alpha\Lambda}.$$

Theory

The required dipole matrix elements are:

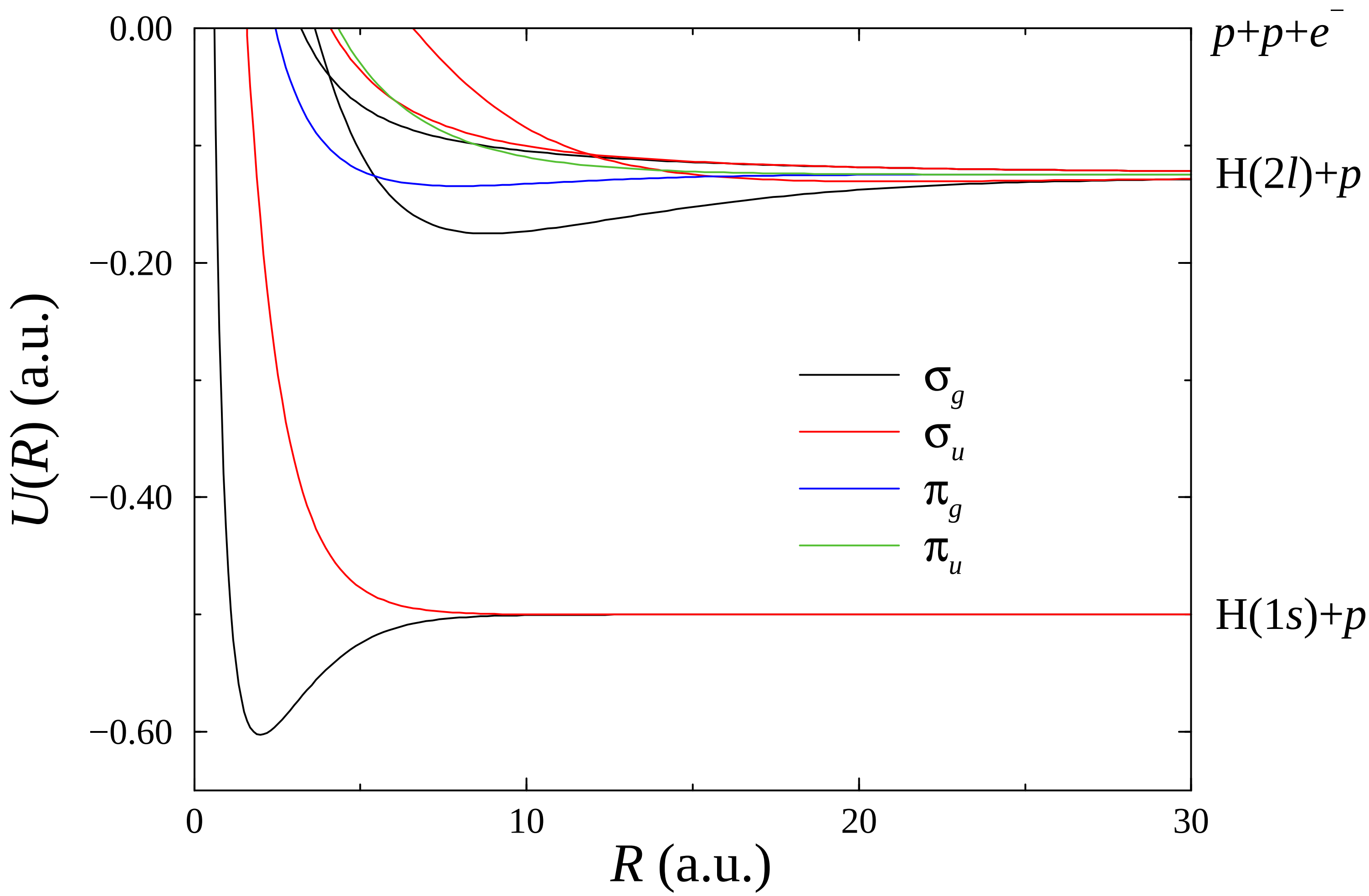
$$\Delta\Lambda = \ 0: \quad \langle\alpha'\Lambda'|d_{\|}|\alpha\Lambda\rangle = \frac{Z_B m_A - Z_A m_B}{m_{AB}} R \ \delta_{\alpha'\alpha}\delta_{\Lambda'\Lambda} - \frac{m_{AB}+Z_{AB}}{m_{AB}+1}\langle\alpha'\Lambda'|z|\alpha\Lambda\rangle\delta_{\Lambda'\Lambda}$$

$$\Delta\Lambda = \pm 1: \quad \langle\alpha'\Lambda'|d_{\perp}|\alpha\Lambda\rangle = -\frac{1}{2}\frac{m_{AB}+Z_{AB}}{m_{AB}+1}\langle\alpha'\Lambda'|\rho|\alpha\Lambda\rangle(\delta_{\Lambda'\Lambda+1}+\delta_{\Lambda'\Lambda-1})$$

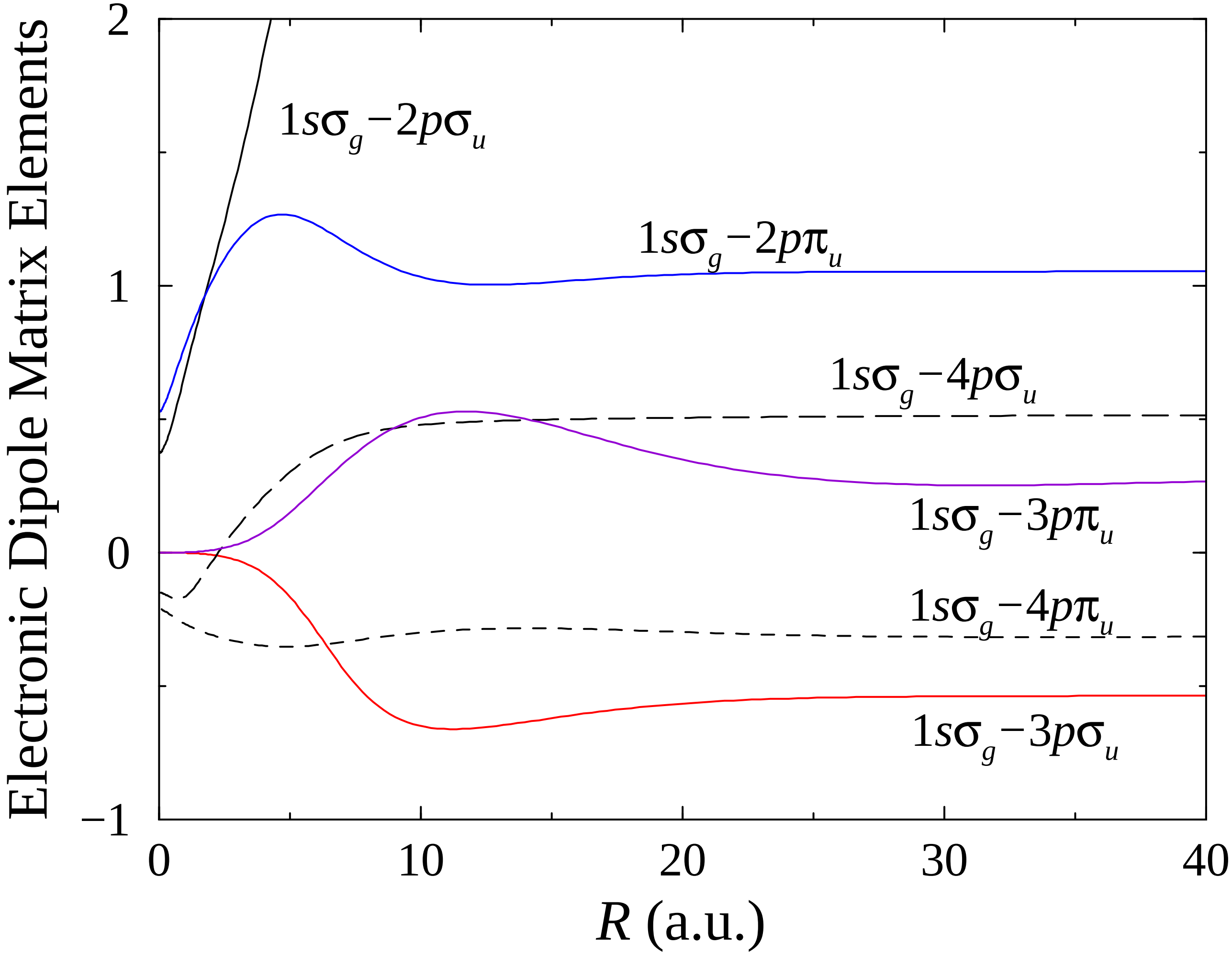
If the molecule is homonuclear, also have: $g \rightarrow u$ and $u \rightarrow g$

H_2^+ Born-Oppenheimer Potentials

($\hbar\omega$=0.058 a.u.=1.5 eV)



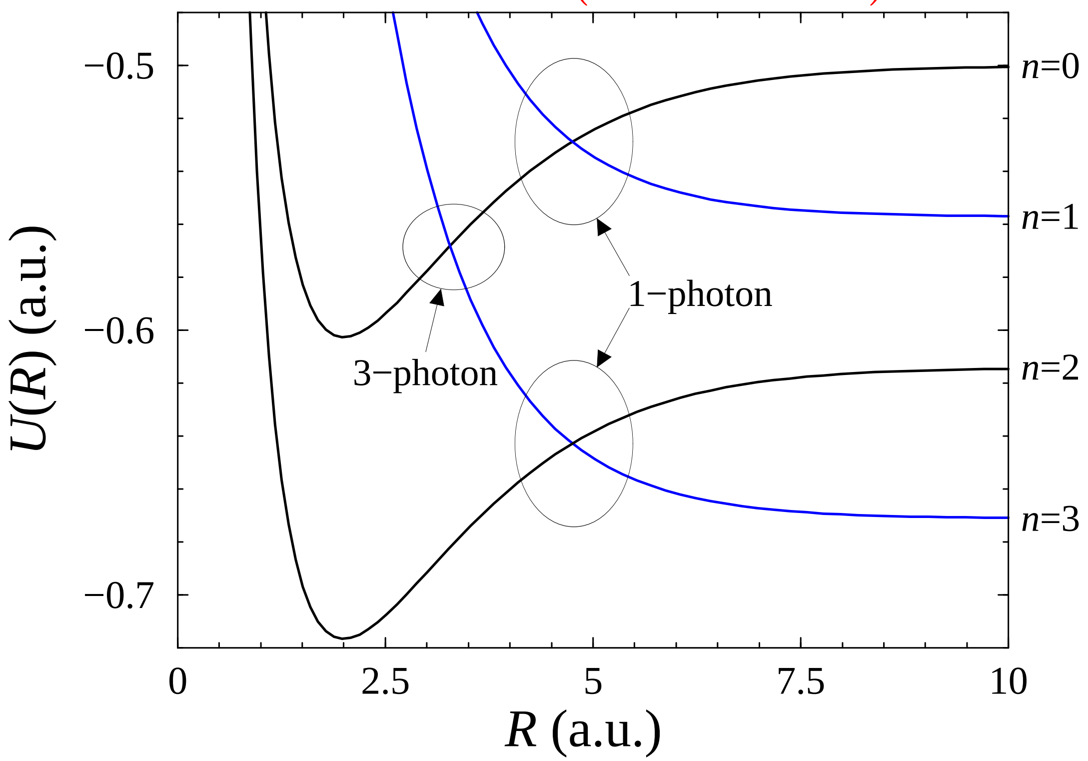
H_2^+ Dipole Matrix Elements



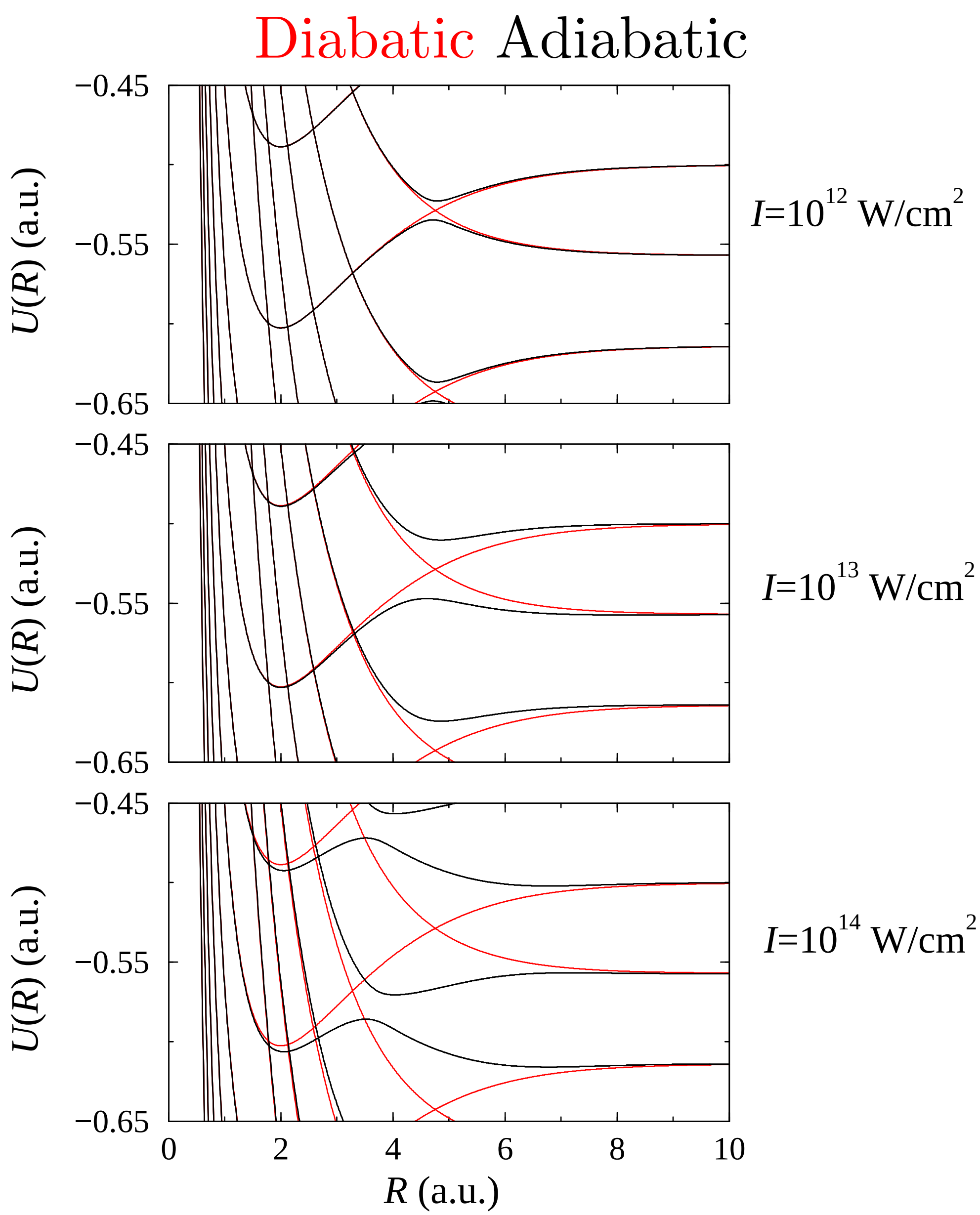
Diabatic Floquet Potentials

$$\left(U^0_{\alpha\Lambda} - n\omega\right) a_{\nu n,\alpha\Lambda} - \frac{1}{2}\sum_{\alpha'\Lambda'} \langle \alpha\Lambda | \mathbf{E}\cdot\mathbf{d} | \alpha'\Lambda' \rangle \left(a_{\nu n-1,\alpha'\Lambda'} + a_{\nu n+1,\alpha'\Lambda'}\right)$$
$$= U_\nu(R,\theta) a_{\nu n,\alpha\Lambda}.$$

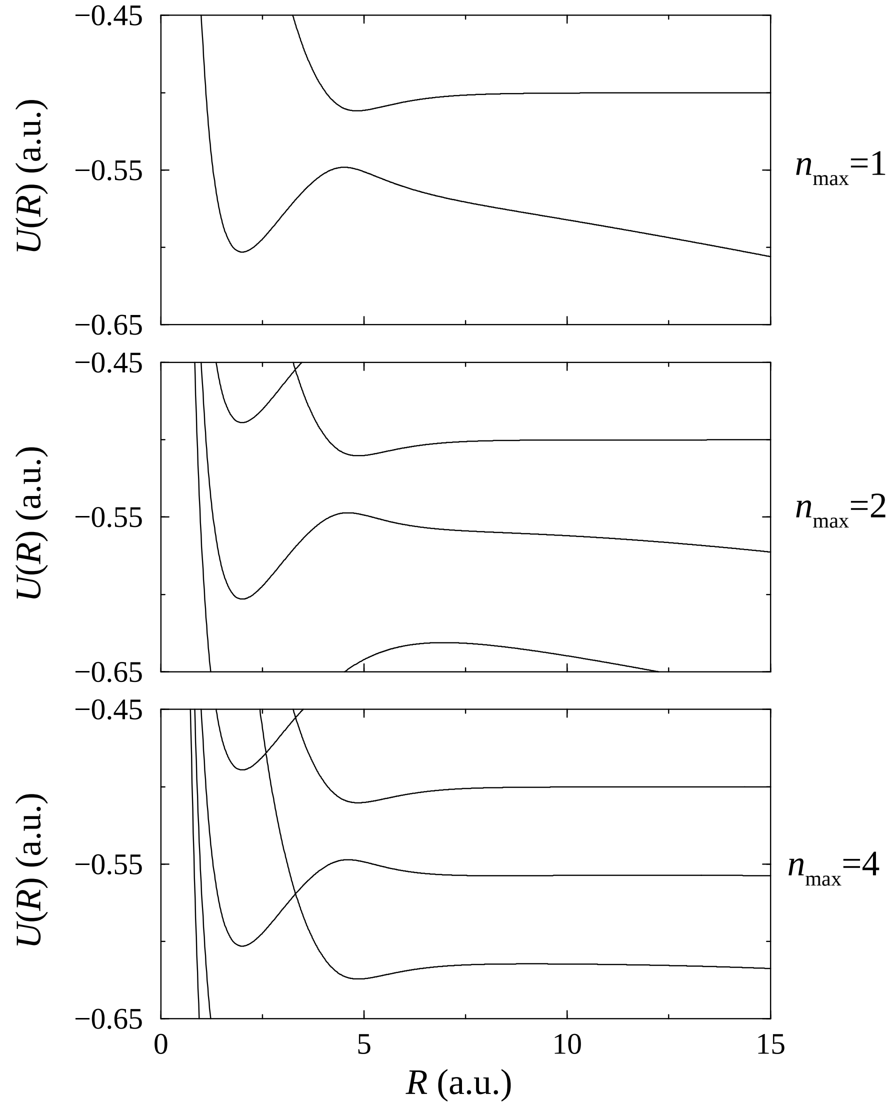
ω=0.058 a.u. (λ=790 nm)



Adiabatic Floquet Potentials

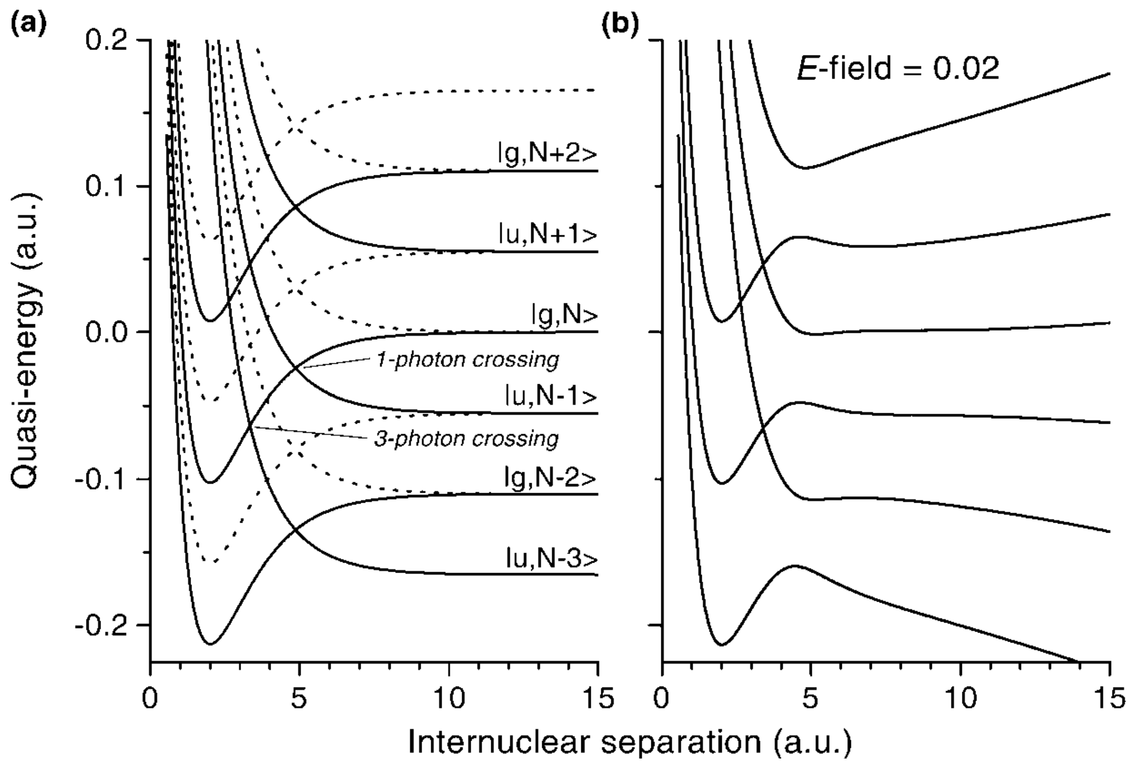


Convergence with Floquet Blocks



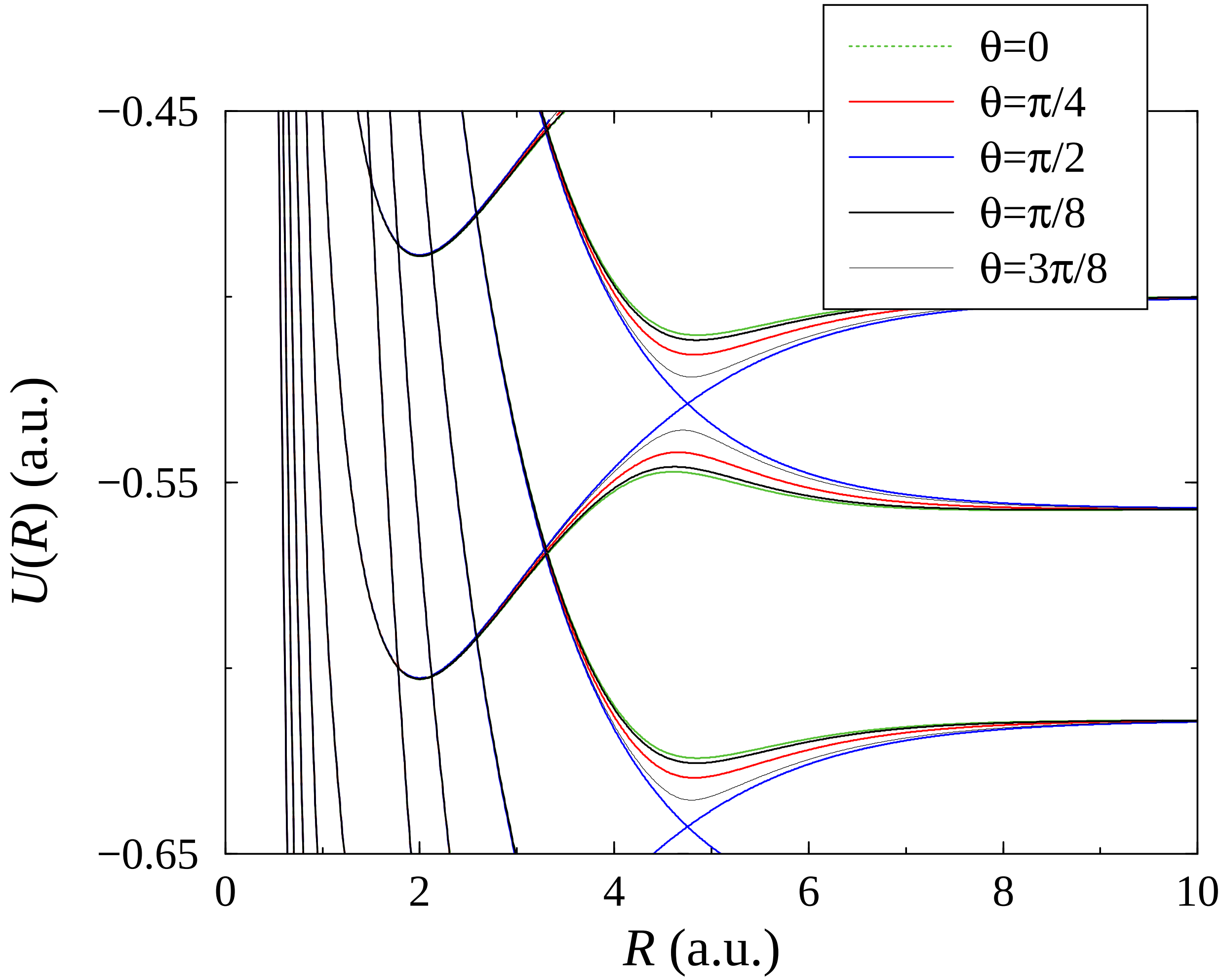
$I = 1 \times 10^{13}$ W/cm^2

Non-Convergence with Floquet Blocks



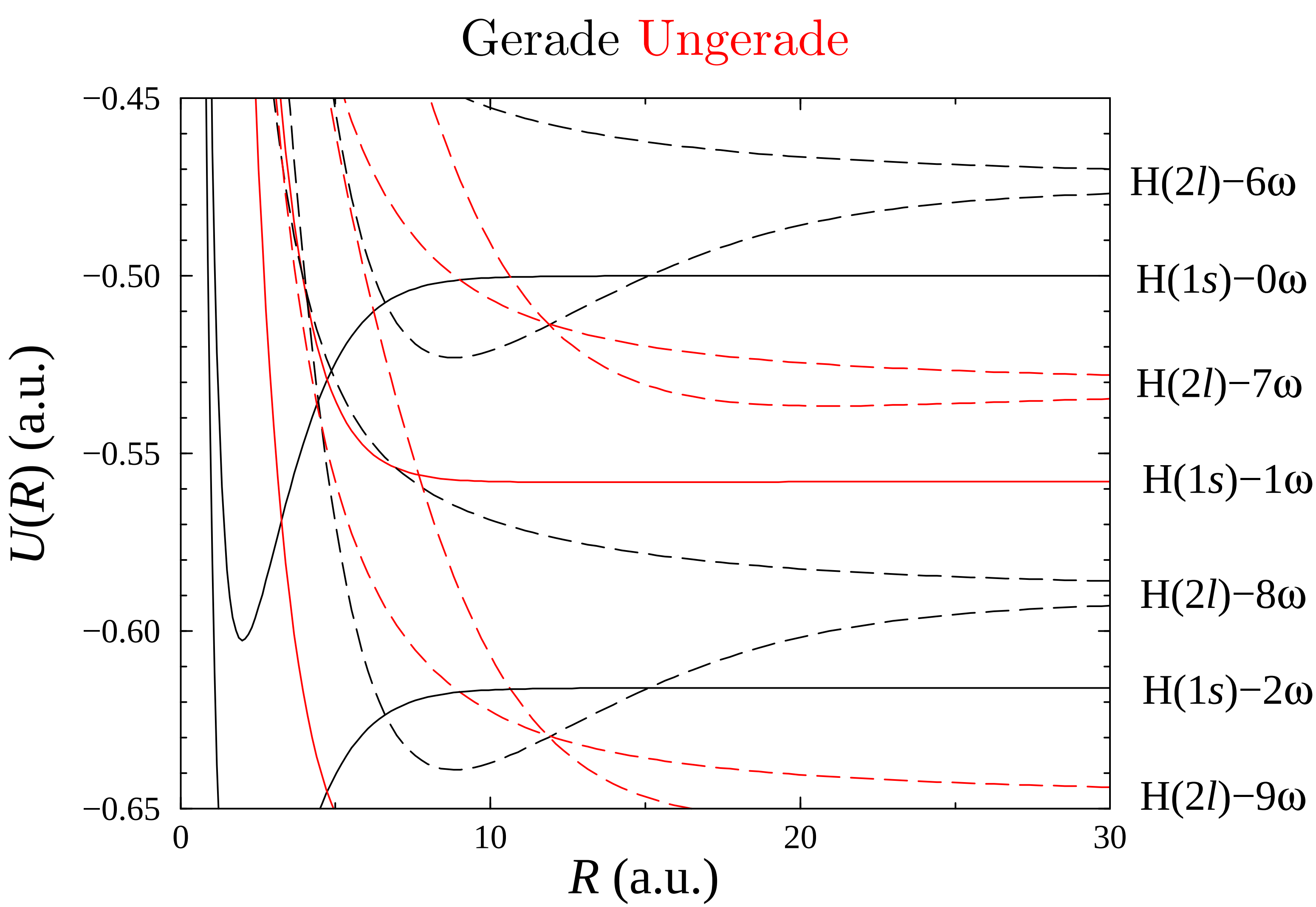
Posthumus, Rep. Prog. Phys. **67**, 623 (2004).

Angle Dependence



$I = 10^{13}$ W/cm^2

Onset of Coupling with n=2

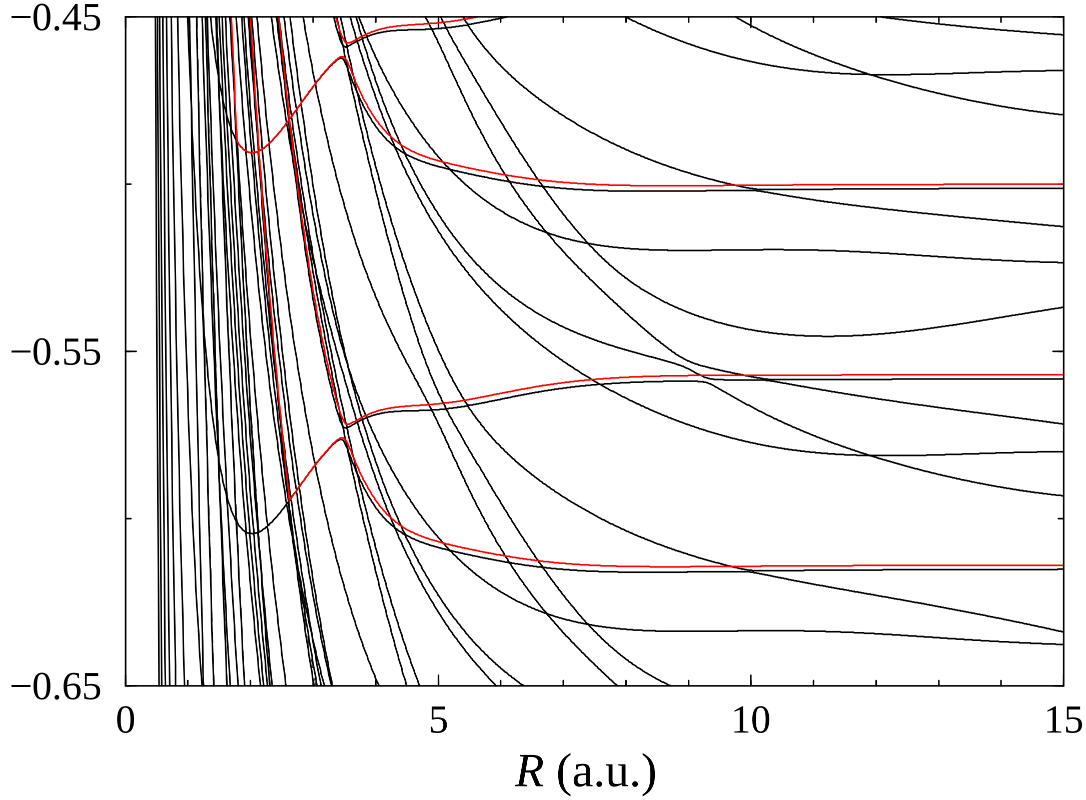


$\theta = 0 \Rightarrow \sigma - \sigma$ coupling only

Onset of Coupling with n=2

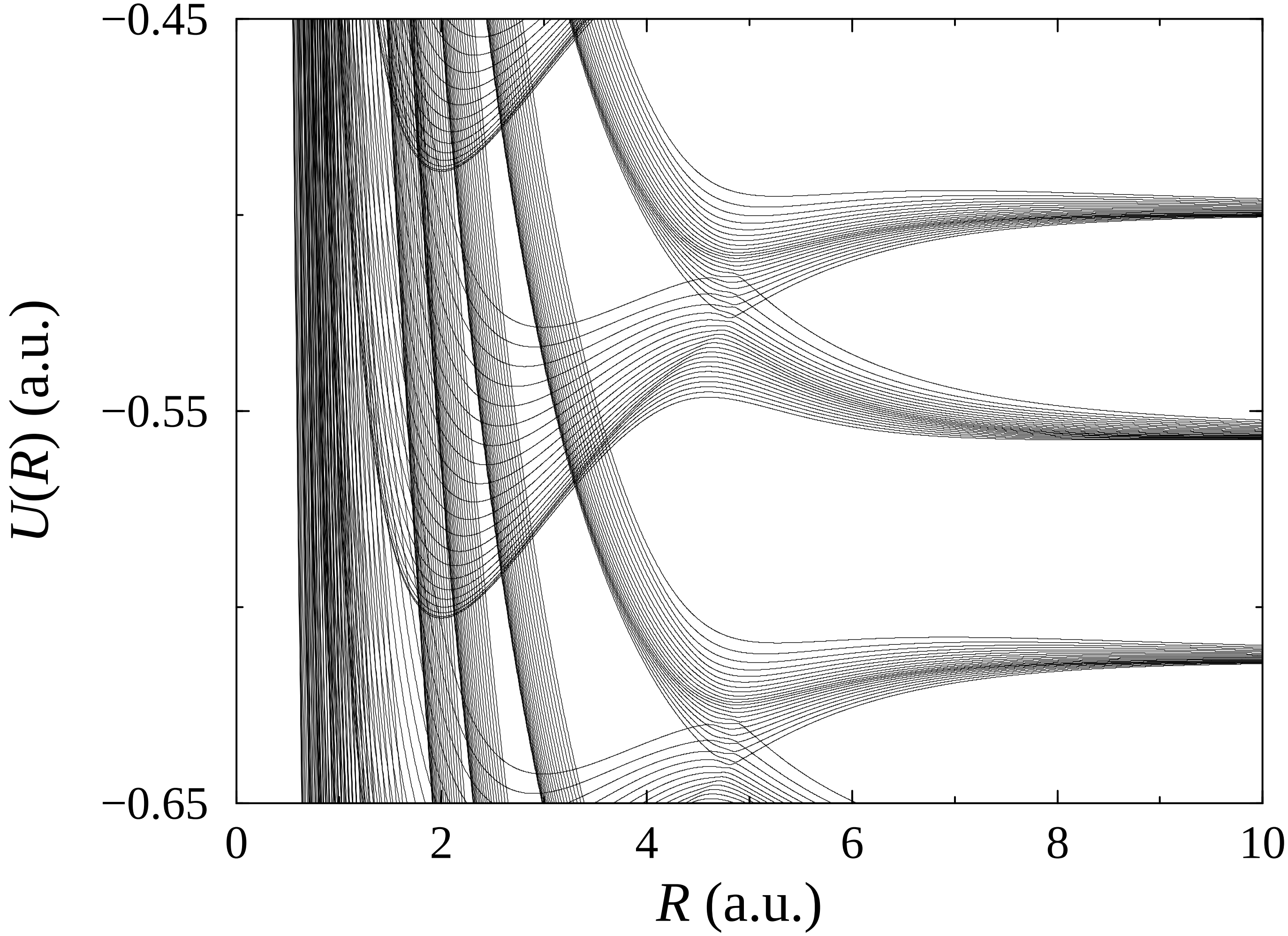
I=5×10^{13} W/cm^2, θ=0

Two-Channels (n=1) Six-Channels (n=2)



Takes 10^{15} W/cm^2 for $\theta=\pi/2$

Including Nuclear Rotation



$J_{\max}=40$, $I=10^{13}$ W/cm^2

Simplest Model

Near 1-photon crossing can simply diagonalize

$$\mathbf{U}(R) = \begin{pmatrix} U_{1s\sigma_g}(R) & \frac{1}{2}RE\cos\theta \\ \frac{1}{2}RE\cos\theta & U_{2p\sigma_u}(R) - \omega \end{pmatrix}$$

when intensities are below about 10^{13} W/cm^2

Summary

- Be careful looking at Floquet curves in literature
- Two-channel model valid mainly for $I < 5 \times 10^{13}$ W/cm^2 or so
- Representation most useful when number of curves is small