Flexible Rydberg aggregates

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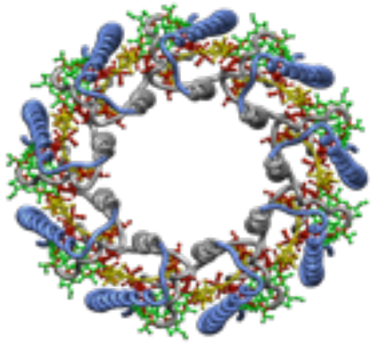
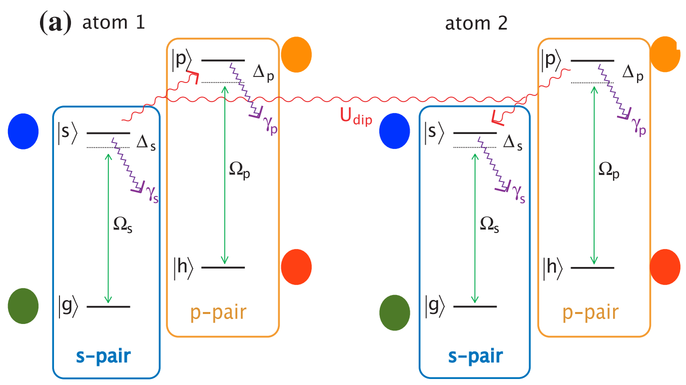
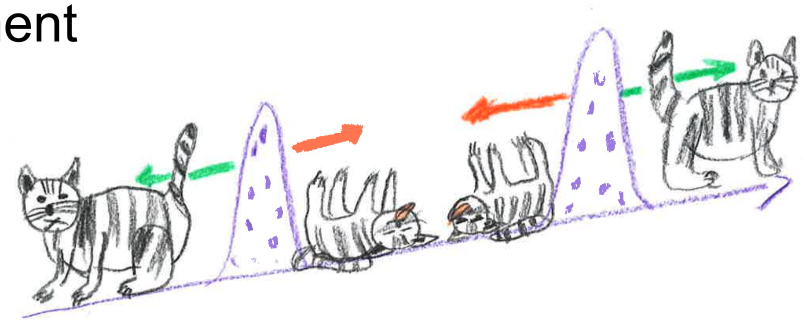
Outline



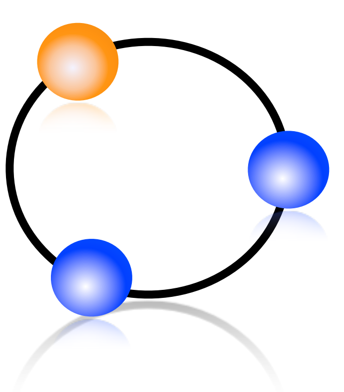
1. Motivation
   (a) Frozen versus unfrozen Rydberg gases, Excitation transport
2. Introduction
   (a) Dipole-dipole excitons and Born-Oppenheimer surfaces
   (b) Van-der Waals interactions
   (c) Dressed dipole-dipole interactions
3. Linked motion and quantum state dynamics
   (a) Schrödinger, Tully and Ehrenfest



4. Entanglement
   (a) Exciton Bell states, entanglement transport and measurement
   (b) Entangled motion and quantum state



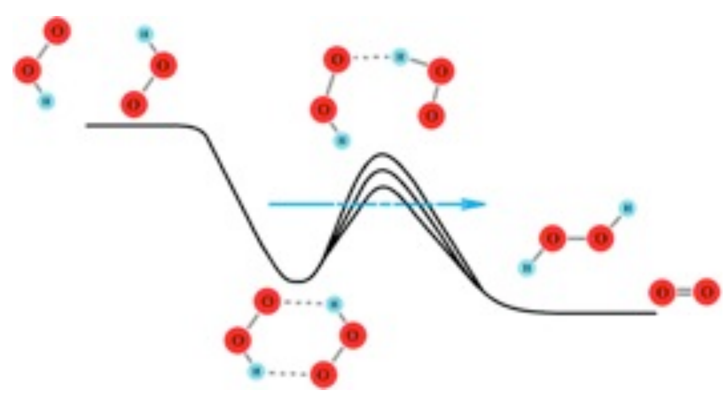
5. Rydberg physics meets Biology
   (a) Excitation transport in Molecular and Rydberg aggregates
6. Rydberg physics meets chemistry
   (a) Rydberg molecules
   (b) Conical Intersections in aggregates

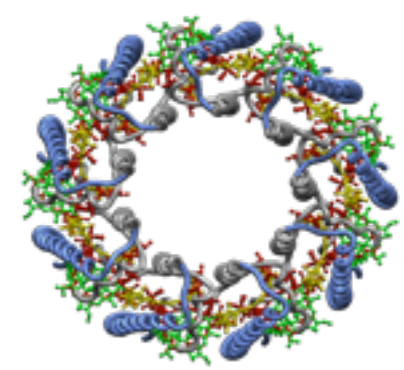


7. Summary

(I) Motivation

(Unfrozen Rydberg gases, Excitation transport)





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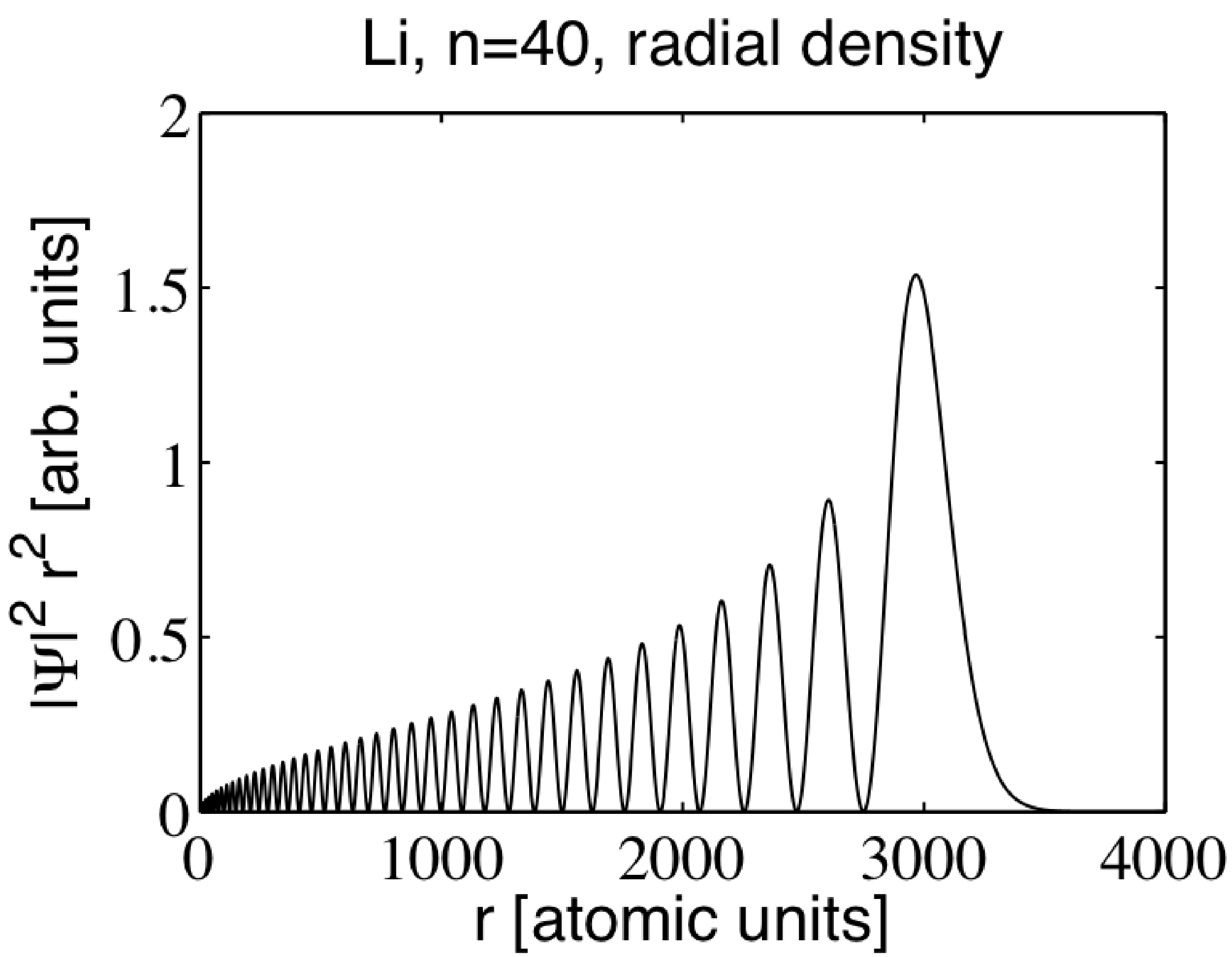
Rydberg atoms

- atoms in states with large principal quantum number n ~ 40-100.
- Large size ~ n^2 (85nm for n=40)
- Large polarizability ~ n^7
- Long life times ~ n^3 (40µs for n=40)
- long range interactions
  $C_3 \sim n^4$ dipole-dipole
  $C_6 \sim n^{11}$ Van-der-Waals



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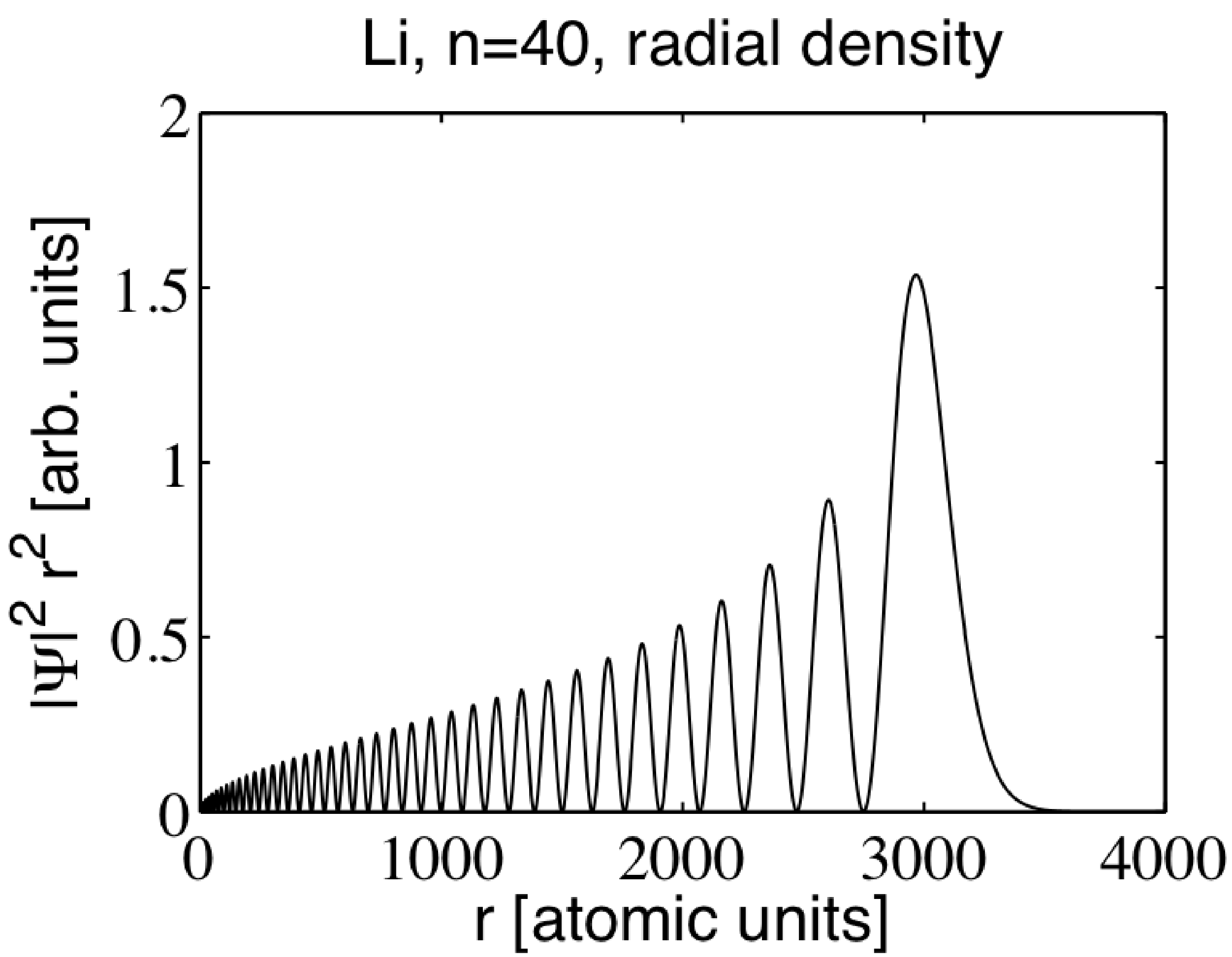
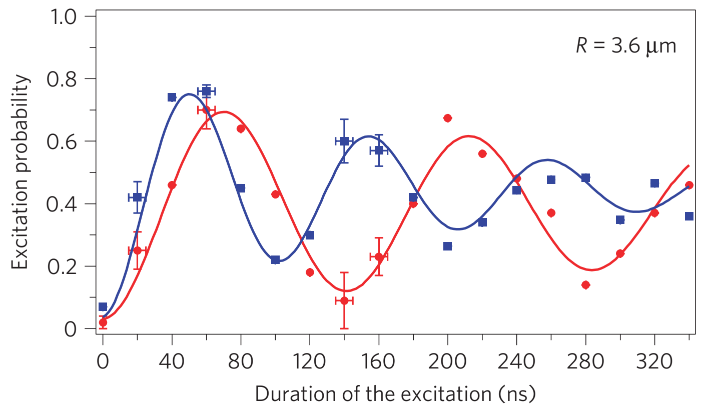


Frozen Rydberg gases

- Rydberg excitation takes <1 μs, experiments can be done faster than atomic motional time-scale: frozen Rydberg gas



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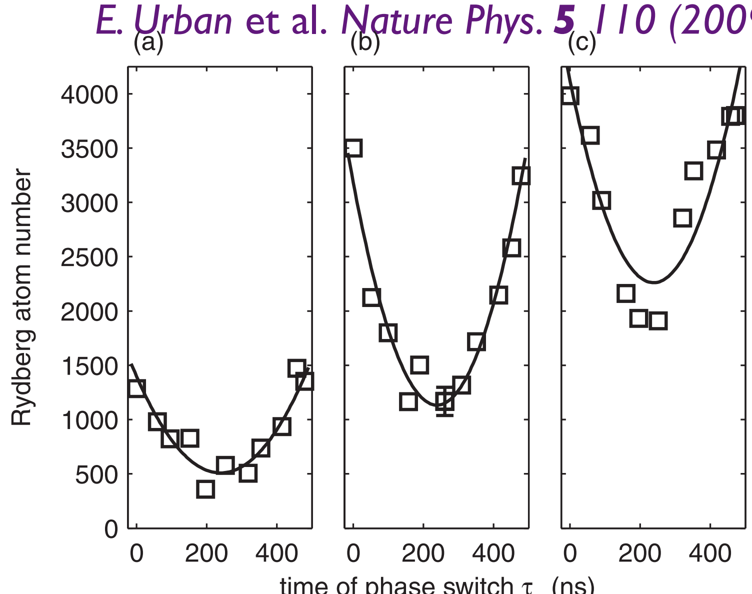

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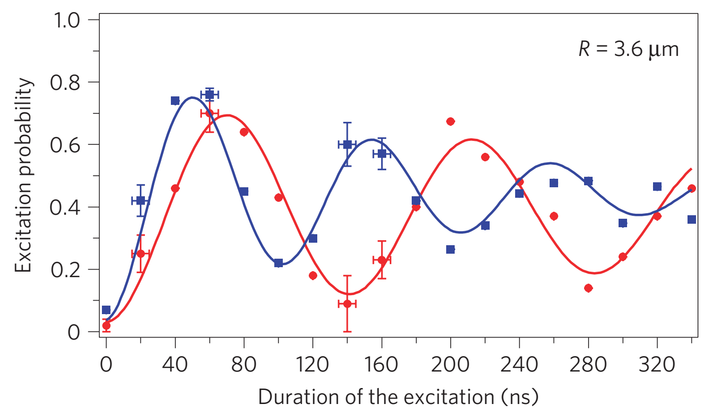

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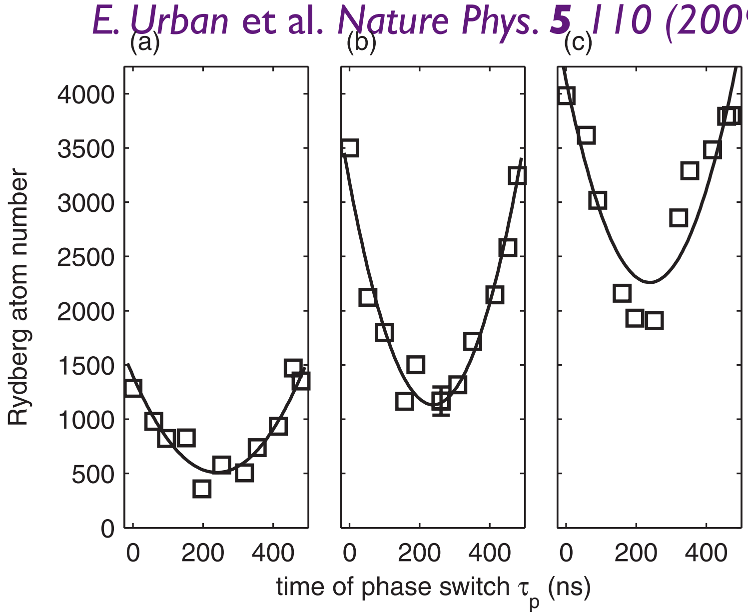

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Example:

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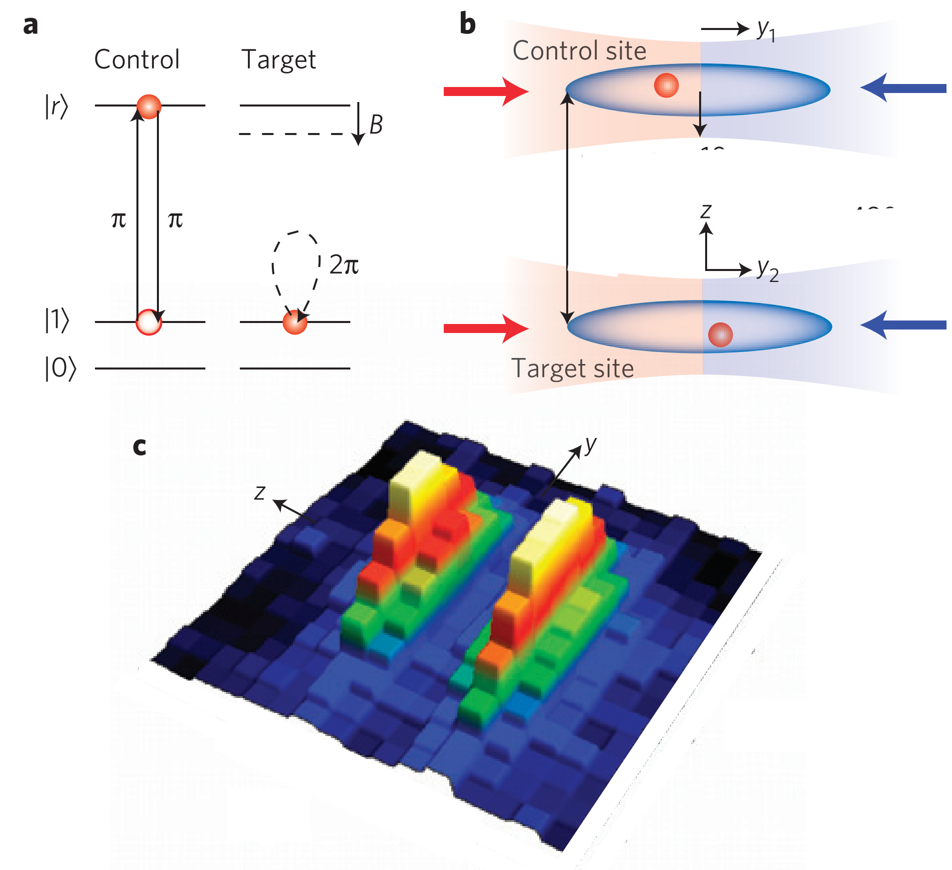
distance d=3.6 μm, t_{exp} =0.3 μs



VdW acceleration ~ 0.3 μm/μs/μs

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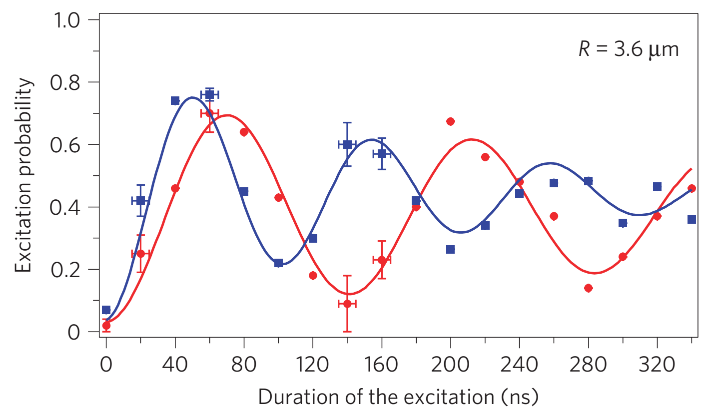

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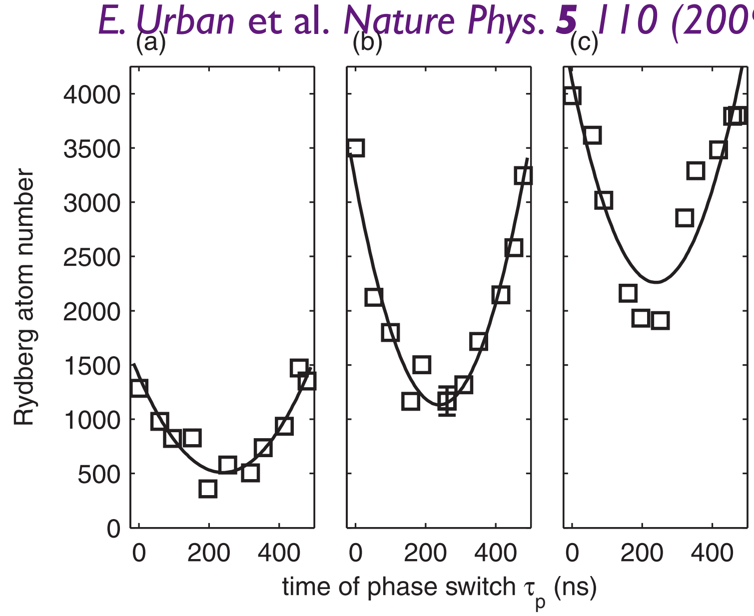

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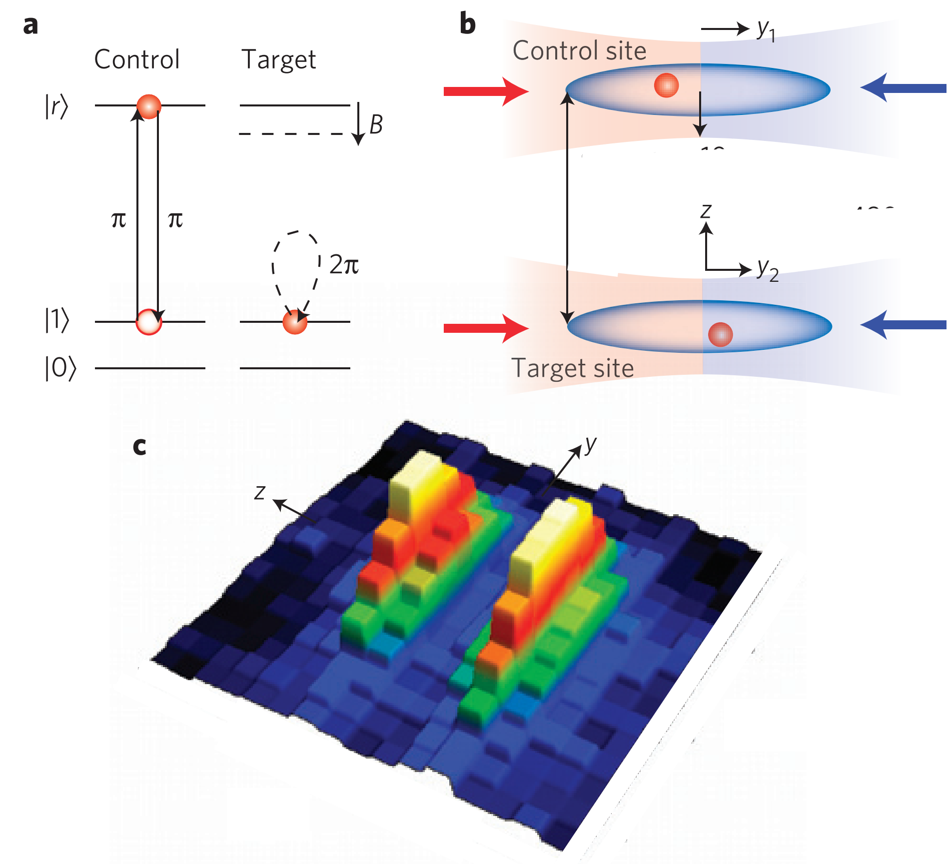
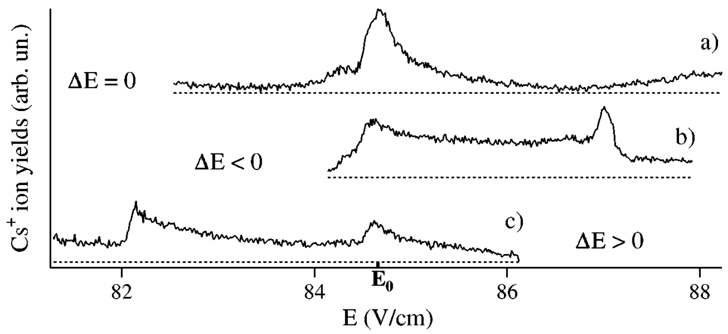


VdW acceleration ~ 0.3 μm/μs/μs

moves ~0.01 μm

“Unfrozen” Rydberg gases

- If we want, we can get them to move *(longer times, higher nryd)*. For light atoms: unfrozen Rydberg gas



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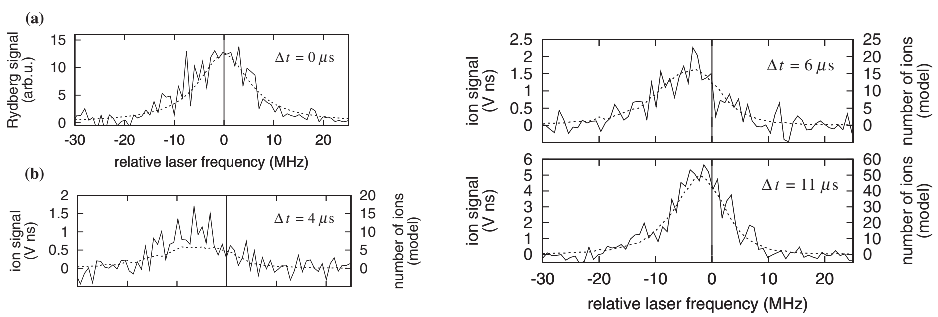
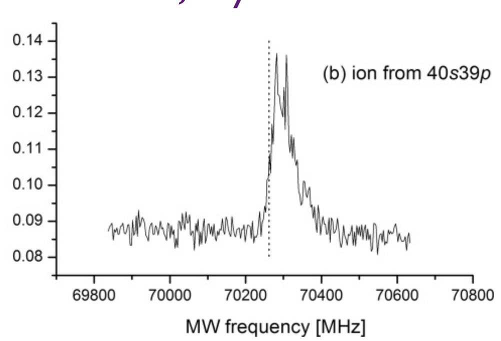


T. Amthor, M. Reetz-Lamour, S. Westermannm J. Denskat and M. Weidemüller; Phys. Rev. Lett. ***98*** *023004 (2007).*



H. Park, E. S. Shuman and T.F. Gallagher; Phys. Rev. A ***84*** *052708 (2011).*

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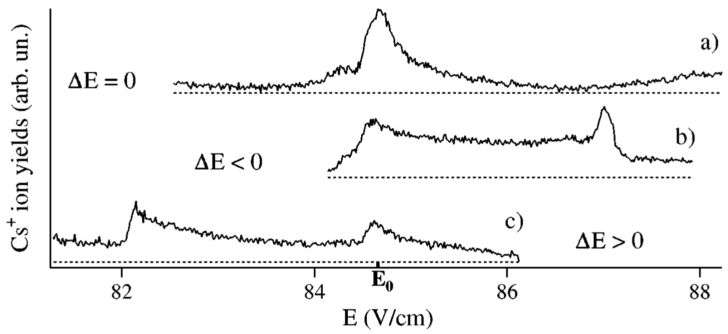

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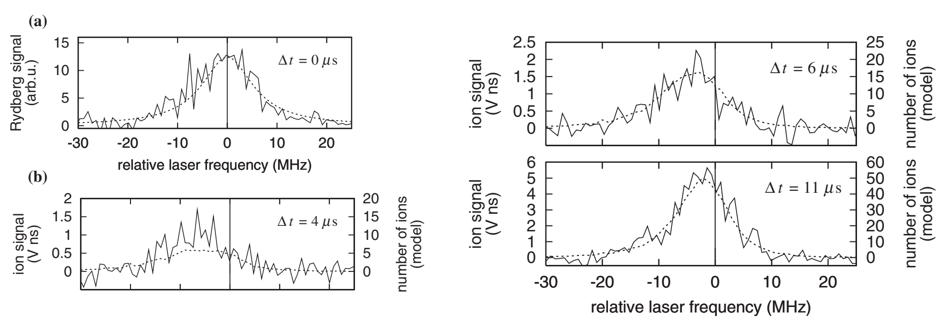

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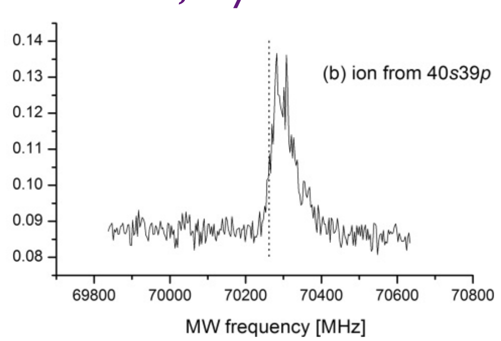

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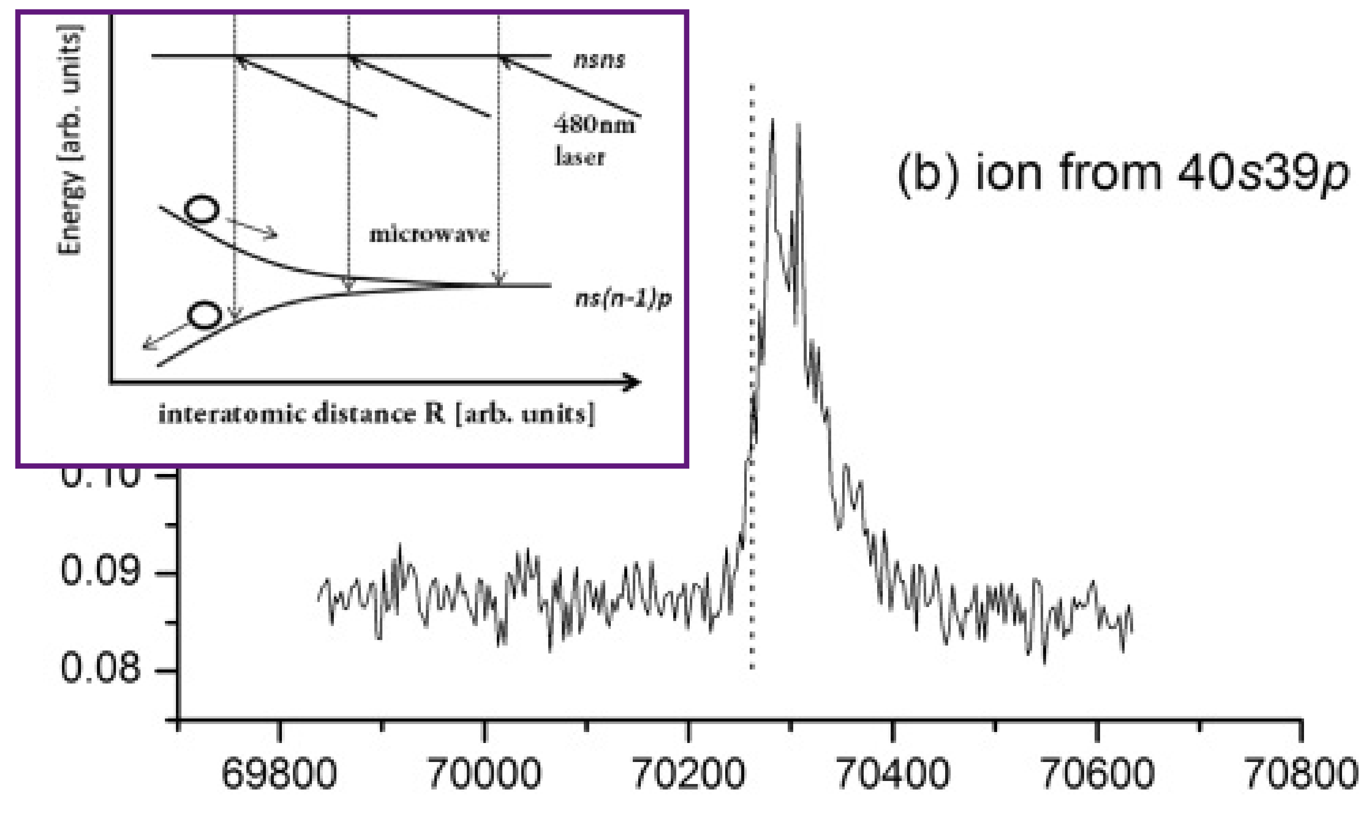

Dip-Dip acceleration ~ 0.17 μm/μs/μs

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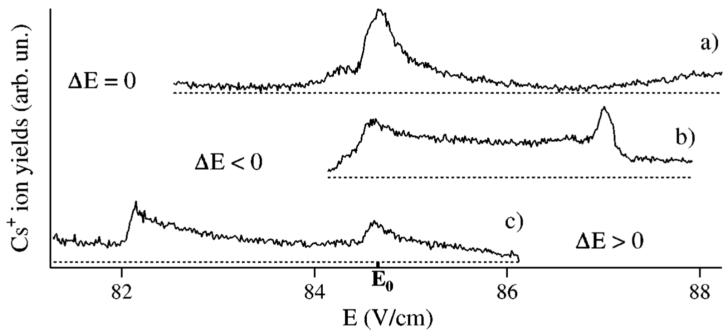

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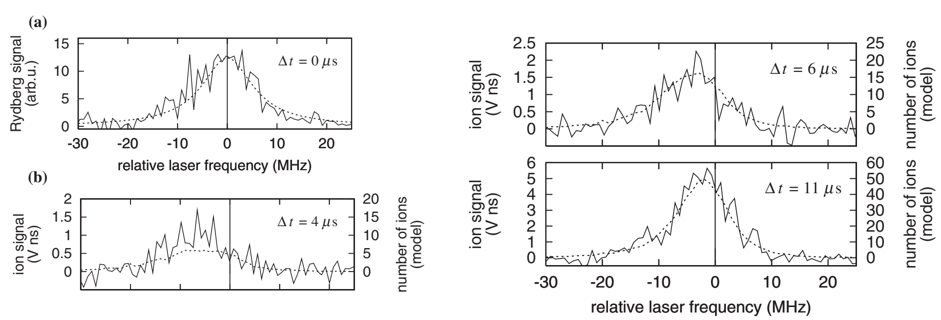

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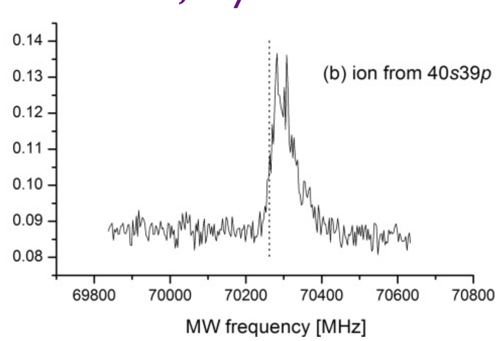

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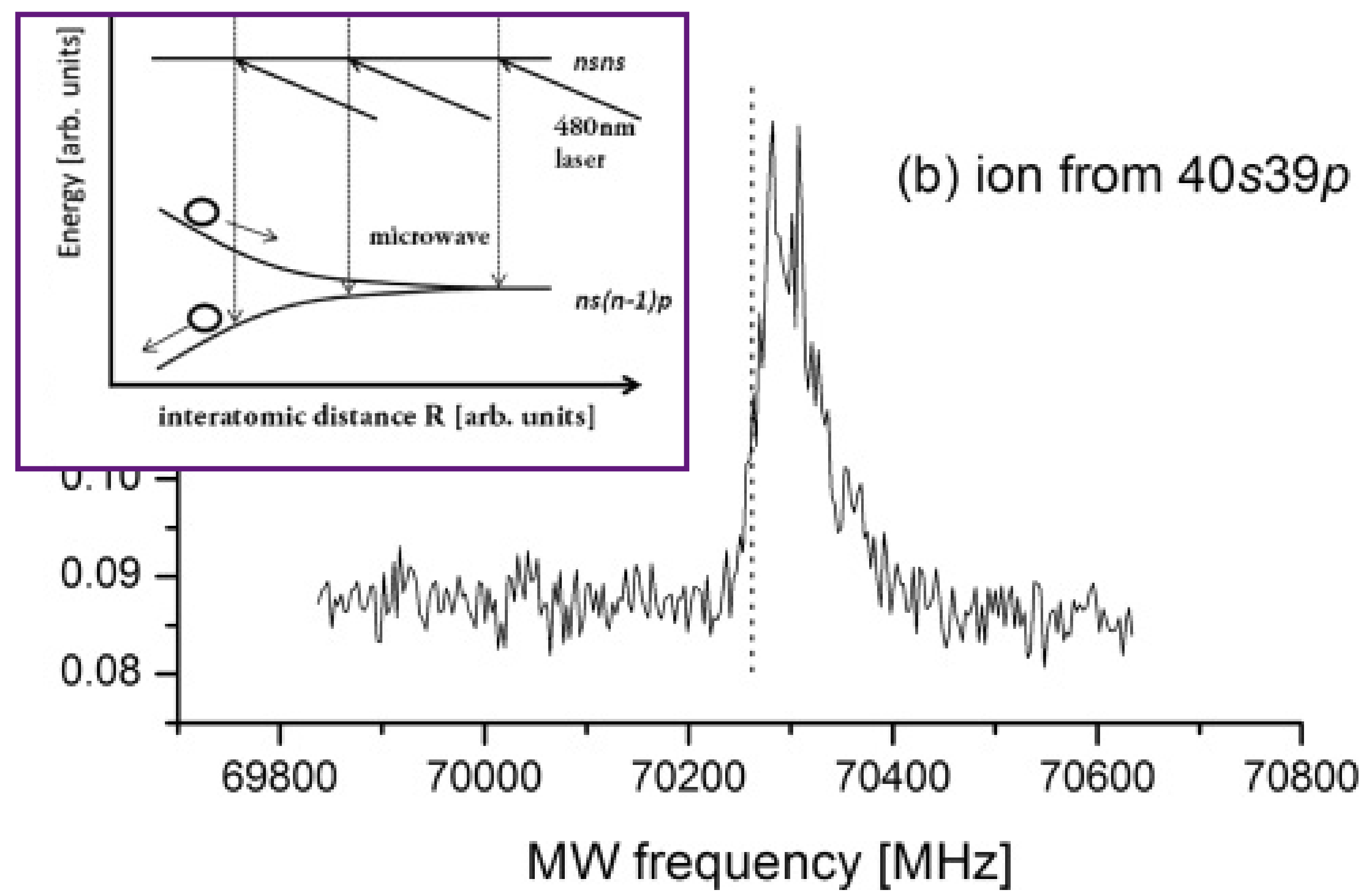


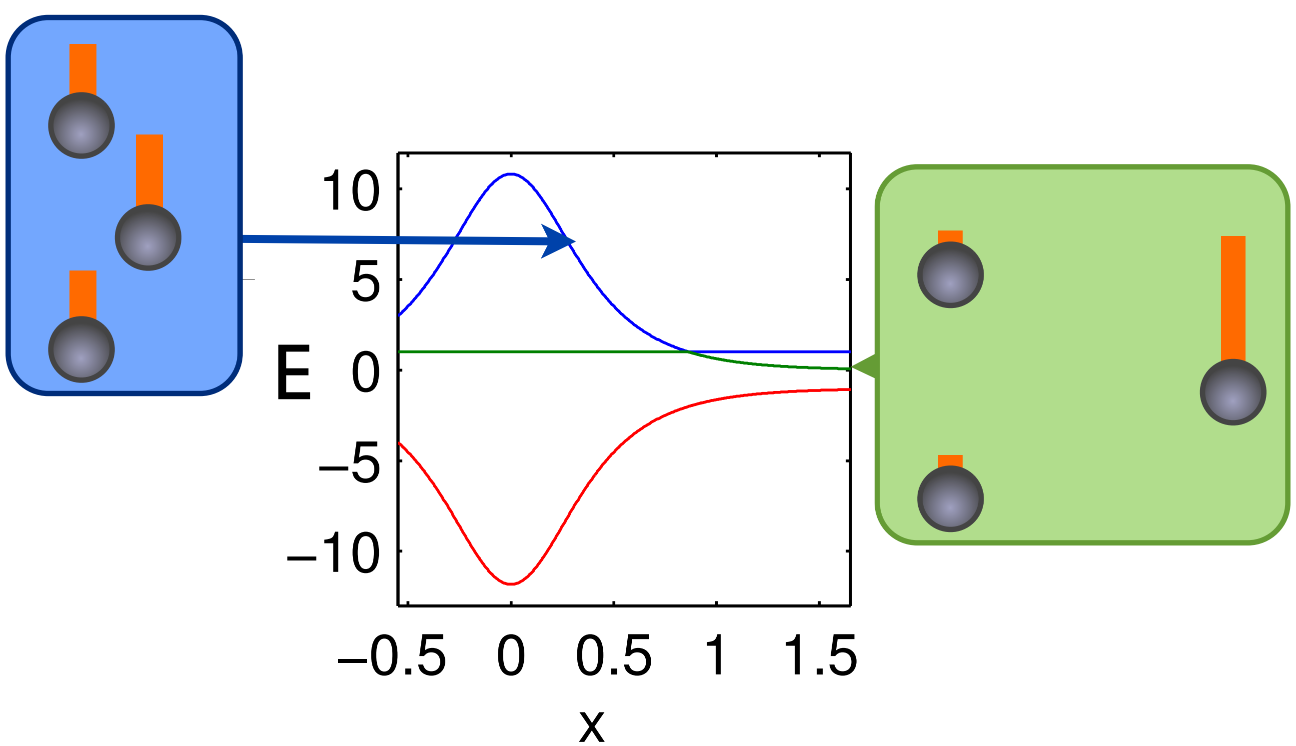
Dip-Dip acceleration ~ 0.17 μm/μs/μs

moves ~3.6 μm

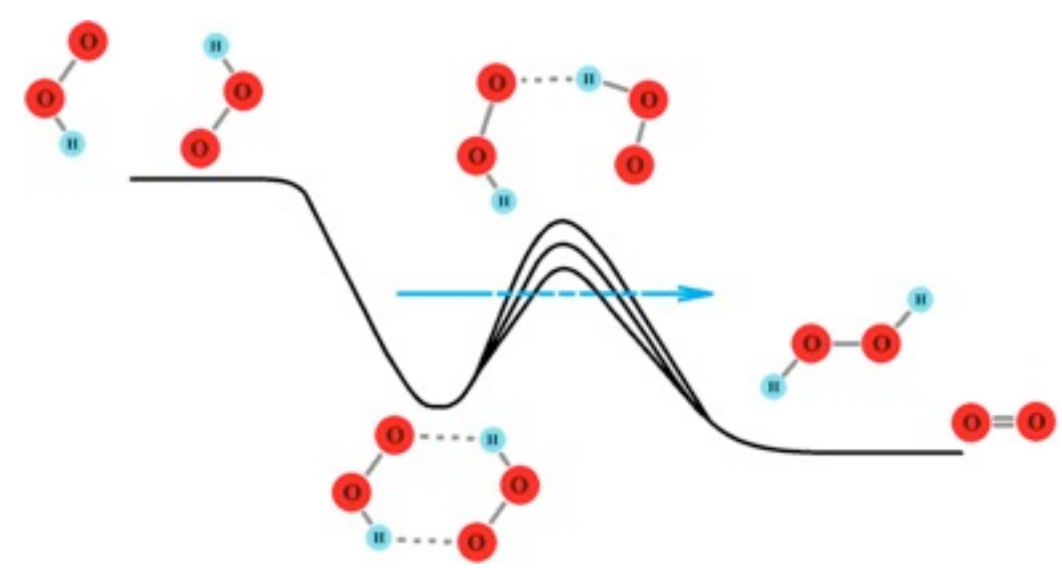
Unfrozen and interacting

- Frozen Rydberg gases/ quantum information: motion causes undesirable decoherence
- Bulk gas: uncontrolled motion often leads to ionization
- Few-body system: coherent motion => chemistry

Rydberg trimer



Chemical reaction



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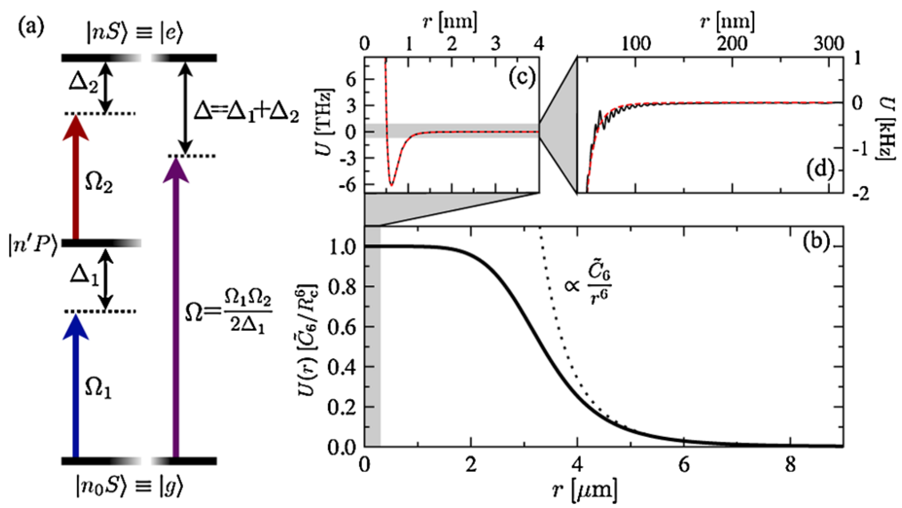
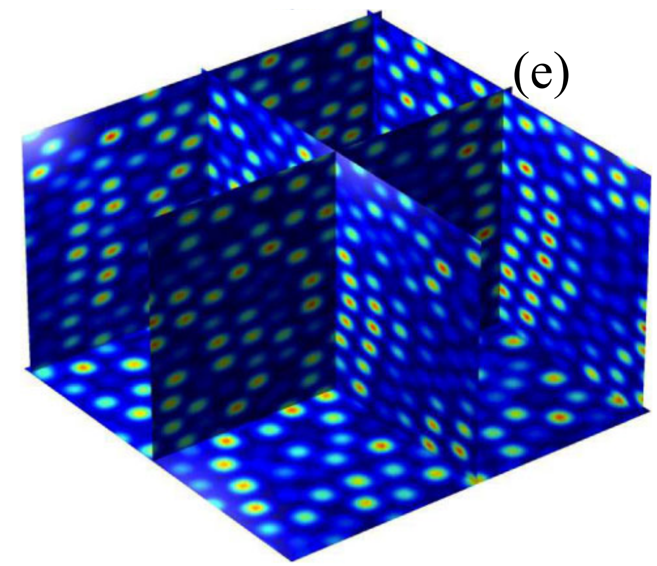
Rydberg dressed gases

- Dressed ultra cold gases





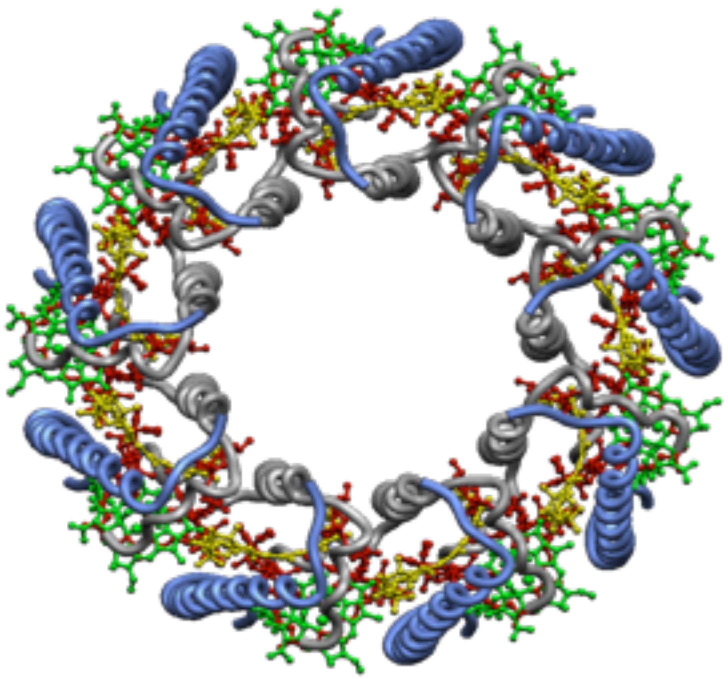
*N. Henkel, R. Nath and T. Pohl, Phys. Rev. Lett. **104** 195302 (2010).*

*G. Pupillo, A. Micheli, M. Boninsegni, I. Lesanovsky and P. Zoller, Phys. Rev. Lett. **104** 223002 (2010).*

- Matches time-scale of motion and decay to that of cold atom traps.

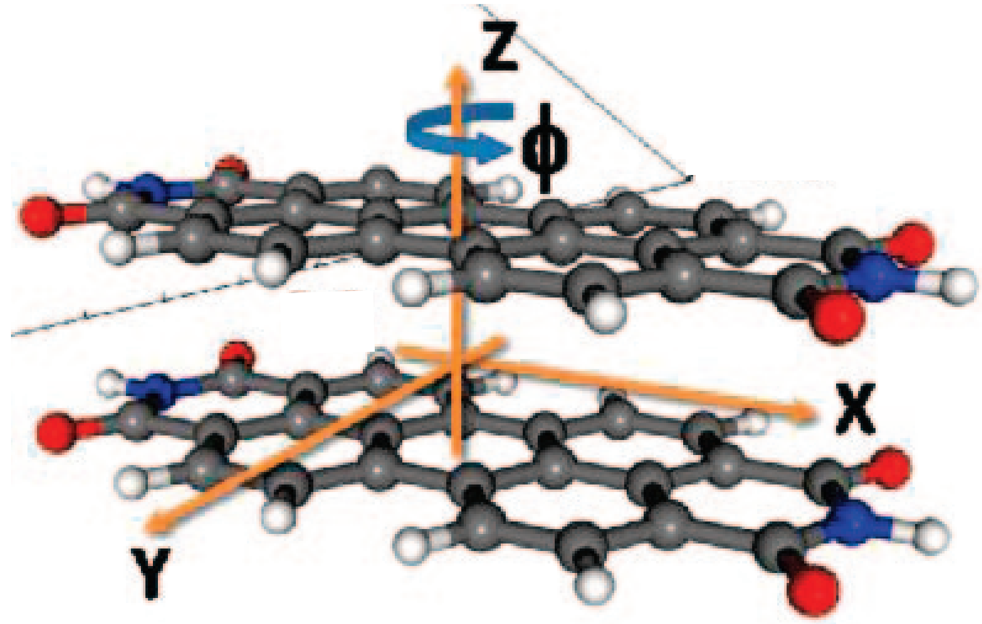
- **Here:** few body viewpoint, can use dressed and un-dressed (bare).

Aggregates and excitation transport



Light-harvesting complex

G. McDermott *et al.*
Nature **374** 517 (1995).



Perylene Bisimide Dye Dimer

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J. Am. Chem. Soc. **130** 12858 (2008).

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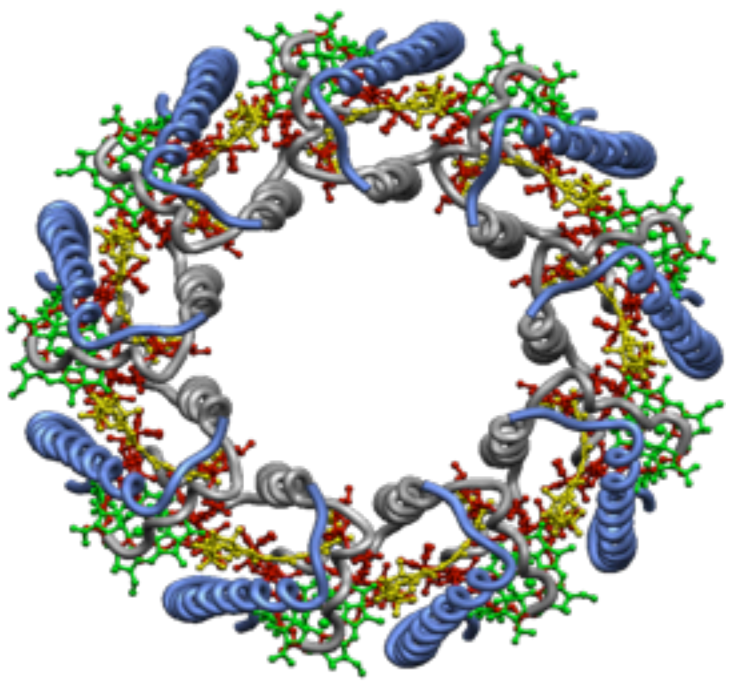

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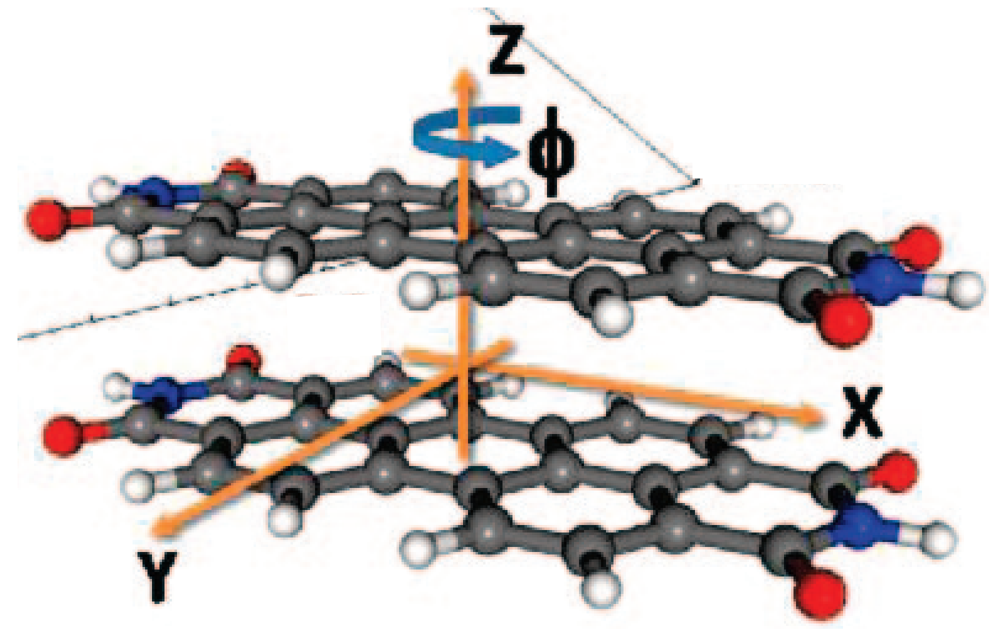

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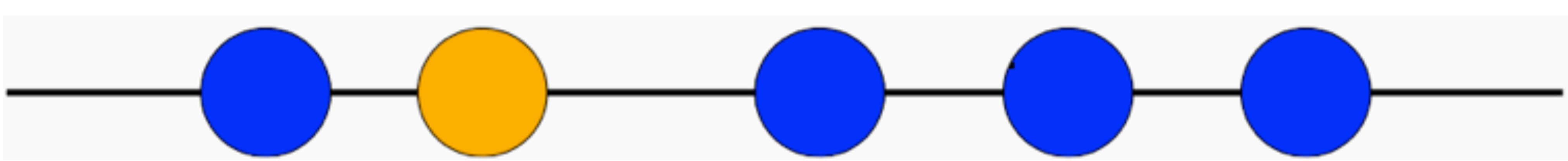

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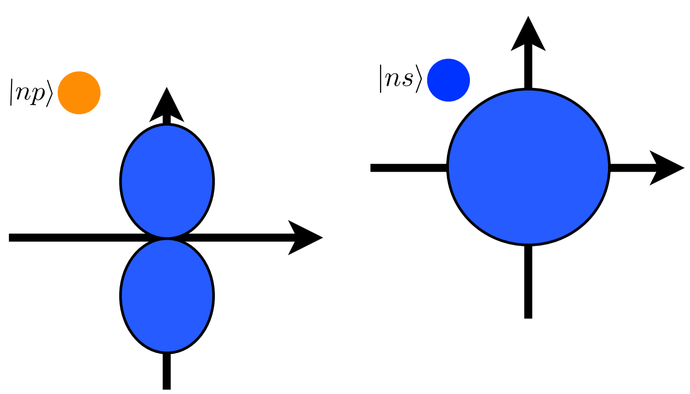
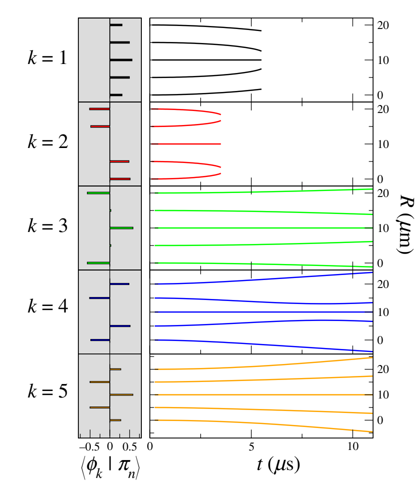
(2) Introduction

(Dipole-dipole and VdW interactions, excitons, BO surfaces, dressed interactions)



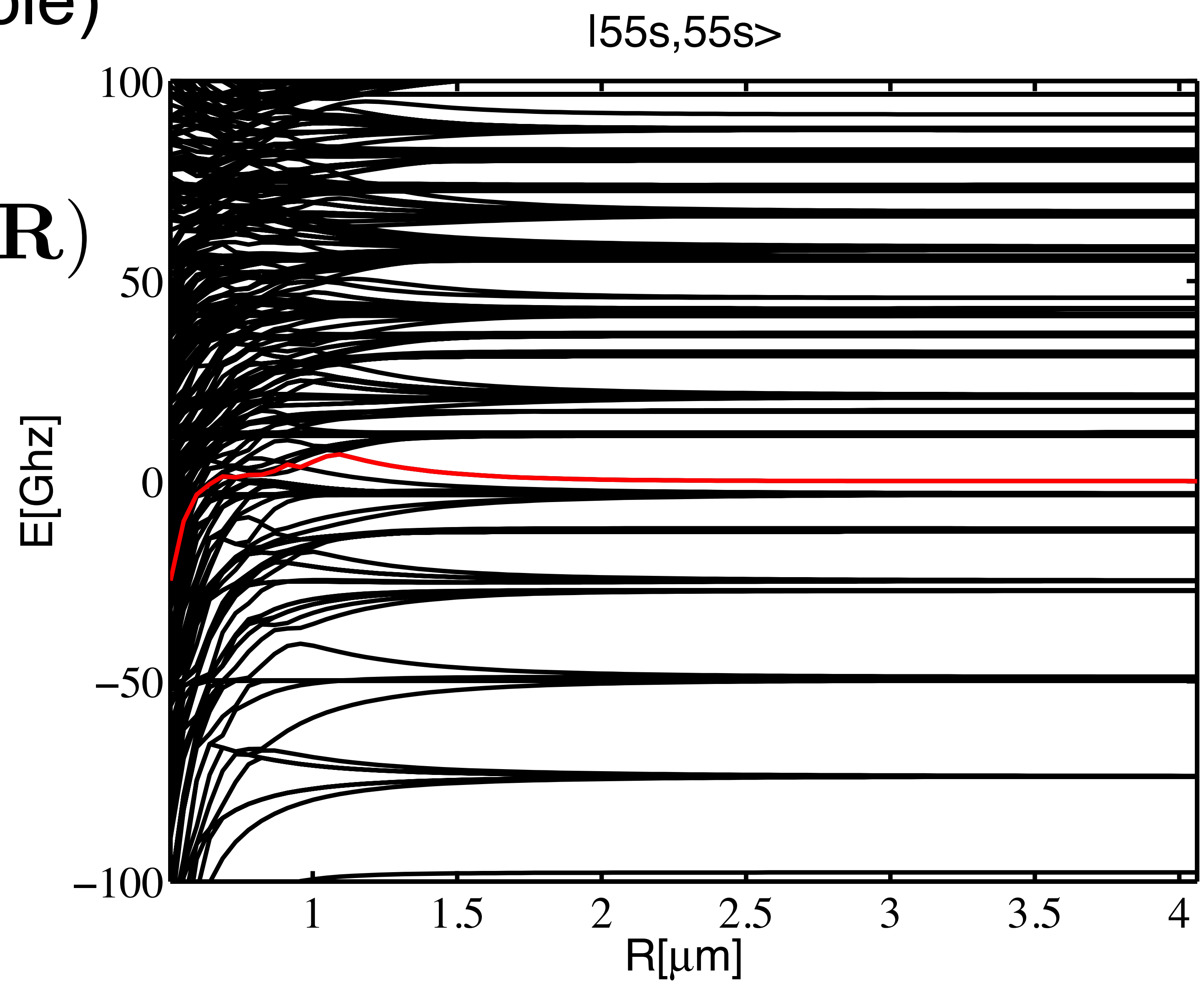


Rydberg interactions

Set up two-atom basis: $|\,\nu_1 j_1 m_1\,\rangle \otimes |\,\nu_2 j_2 m_2\,\rangle$

Determine interaction matrix elements (leading dipole-dipole)

Diagonalize Hamiltonian $\hat{H}(\mathbf{R})$



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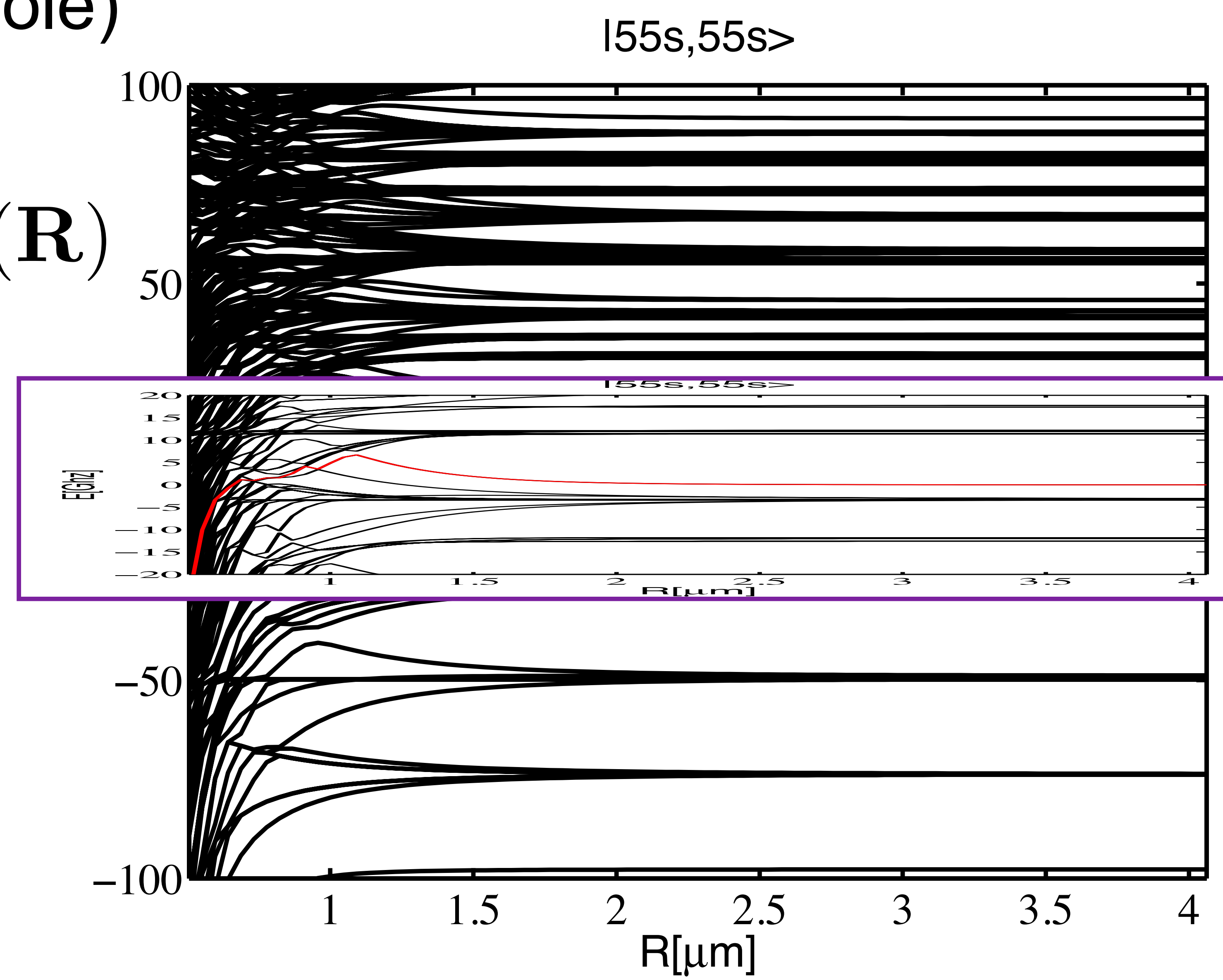

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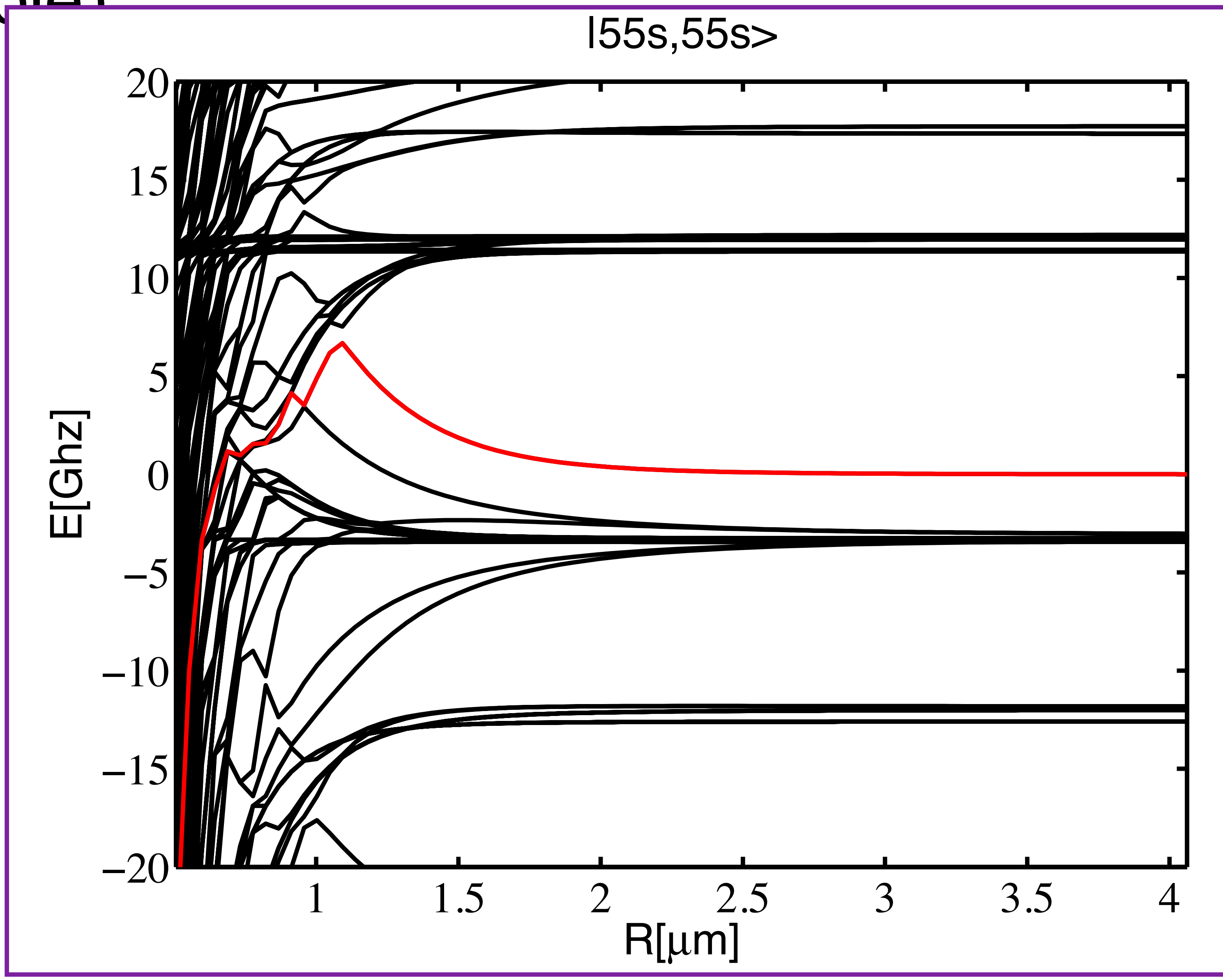
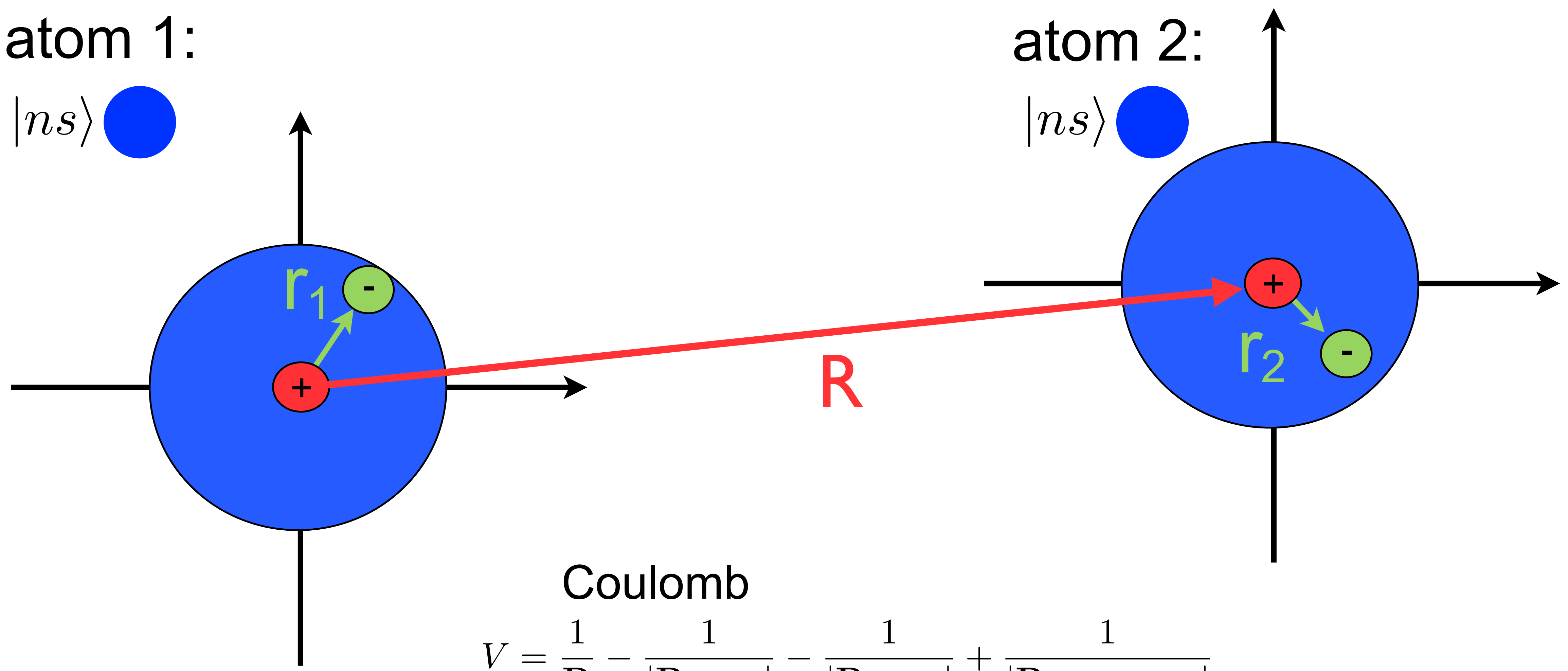


Van-der-Waals interaction



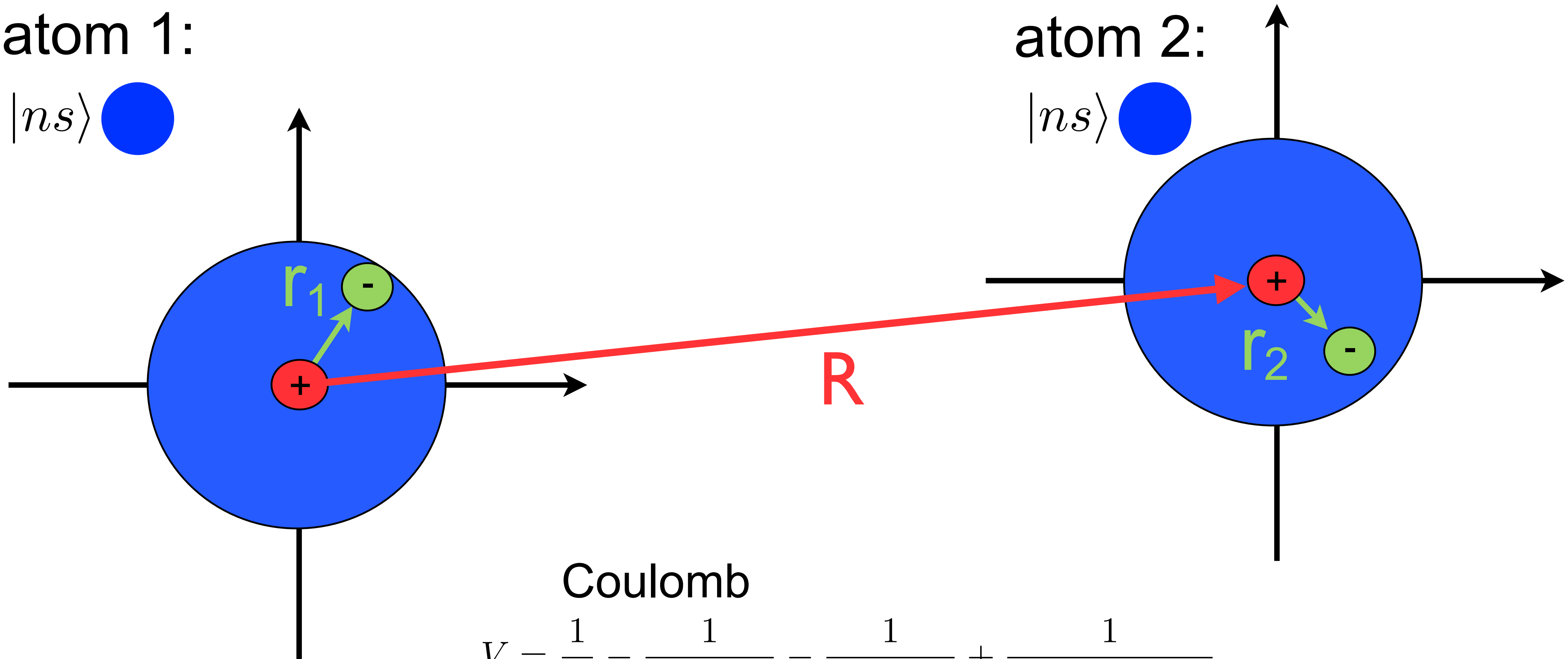
Coulomb

$$V = \frac{1}{\mathbf{R}} - \frac{1}{|\mathbf{R}+\mathbf{r}_2|} - \frac{1}{|\mathbf{R}-\mathbf{r}_1|} + \frac{1}{|\mathbf{R}+\mathbf{r}_2-\mathbf{r}_1|}$$
$$= \frac{\mathbf{r}_1\cdot\mathbf{r}_2 - 3(\mathbf{r}_1\cdot\hat{\mathbf{R}})(\mathbf{r}_2\cdot\hat{\mathbf{R}})}{R^3}$$

No permanent dipole-moment:

$$\langle ns|\langle ns|V|ns\rangle|ns\rangle = 0$$

Van-der-Waals interaction



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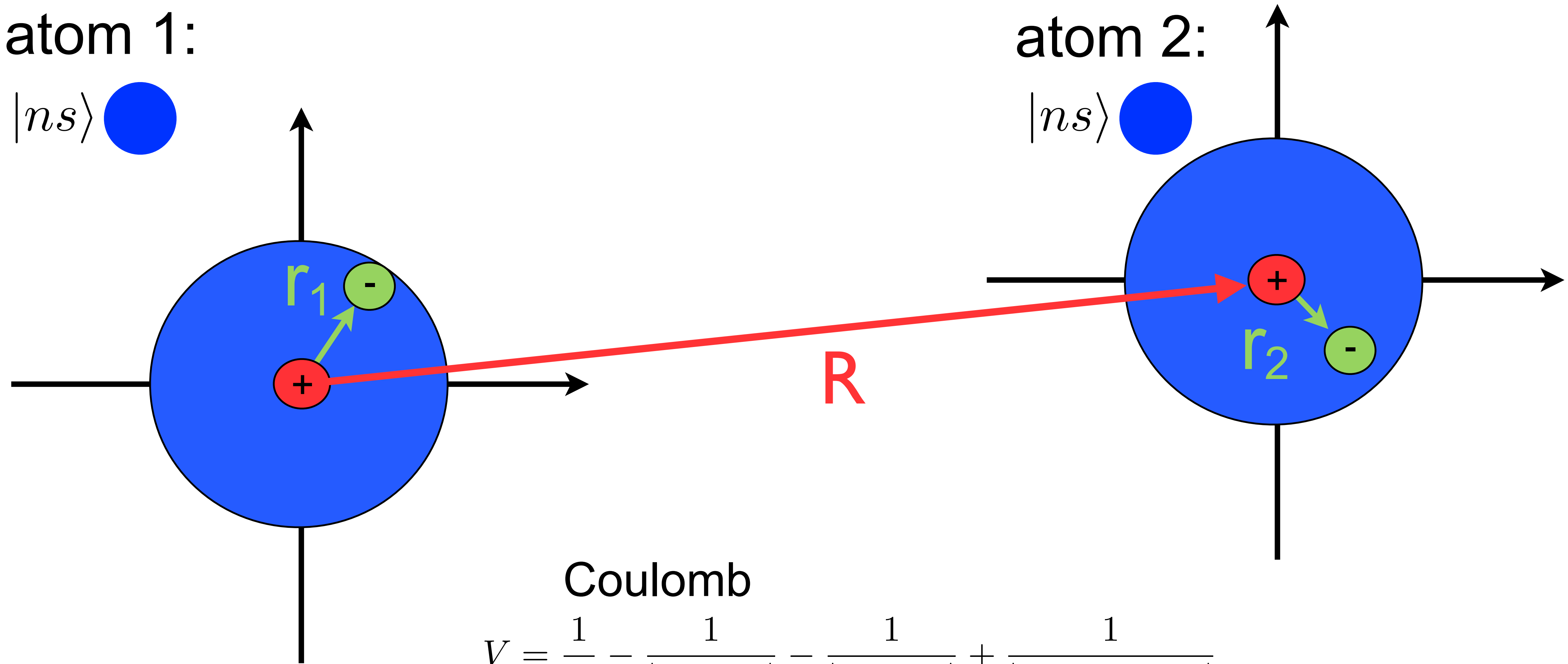
Higher order perturbation theory:

$$E = \langle ns|\langle ns|V\left[\sum_X |X\rangle\langle X|\right]V|ns\rangle|ns\rangle \neq 0$$

Van-der-Waals interaction



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$$V_{\mathrm{VdW}} \sim \frac{1}{R^6}$$

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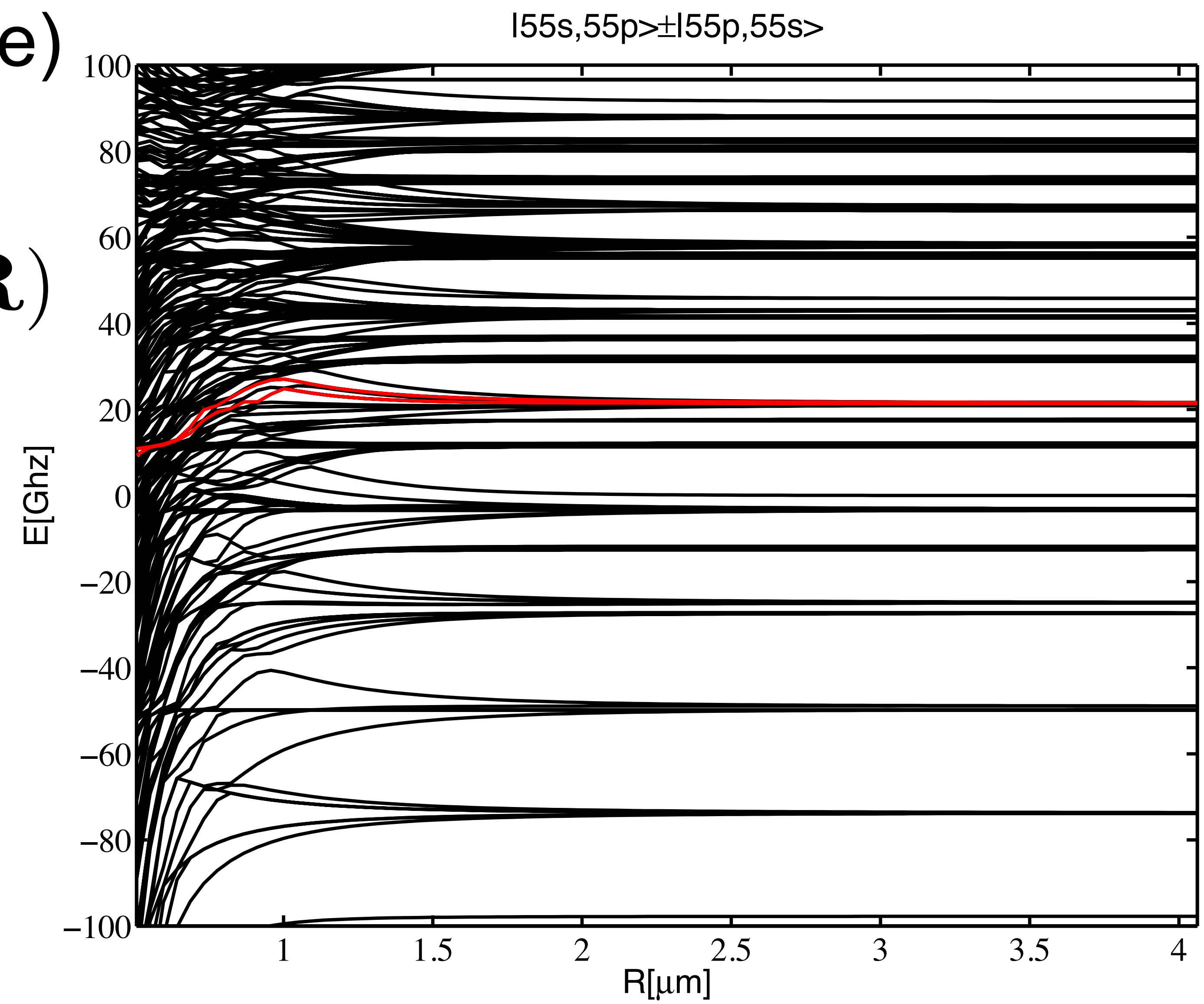

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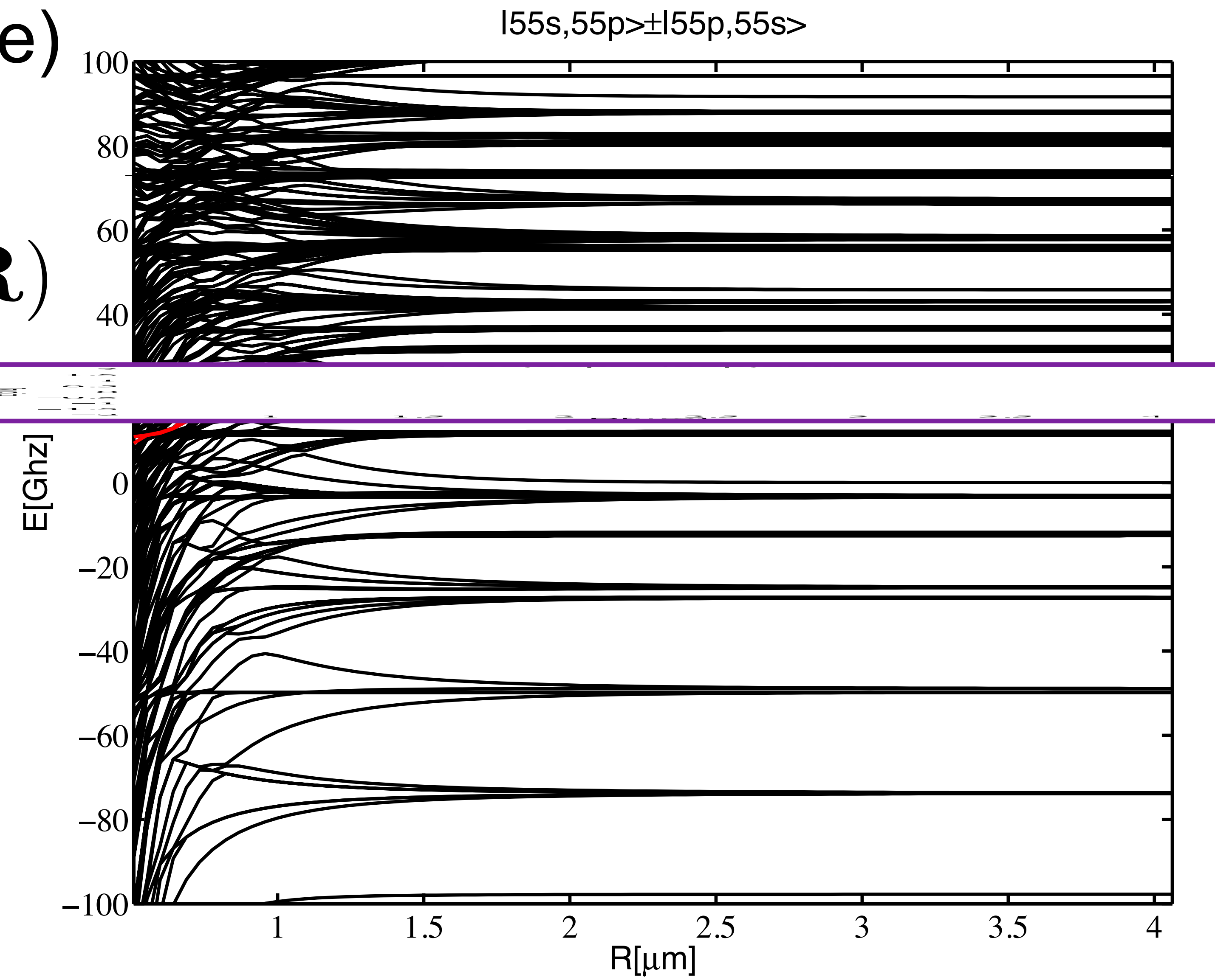

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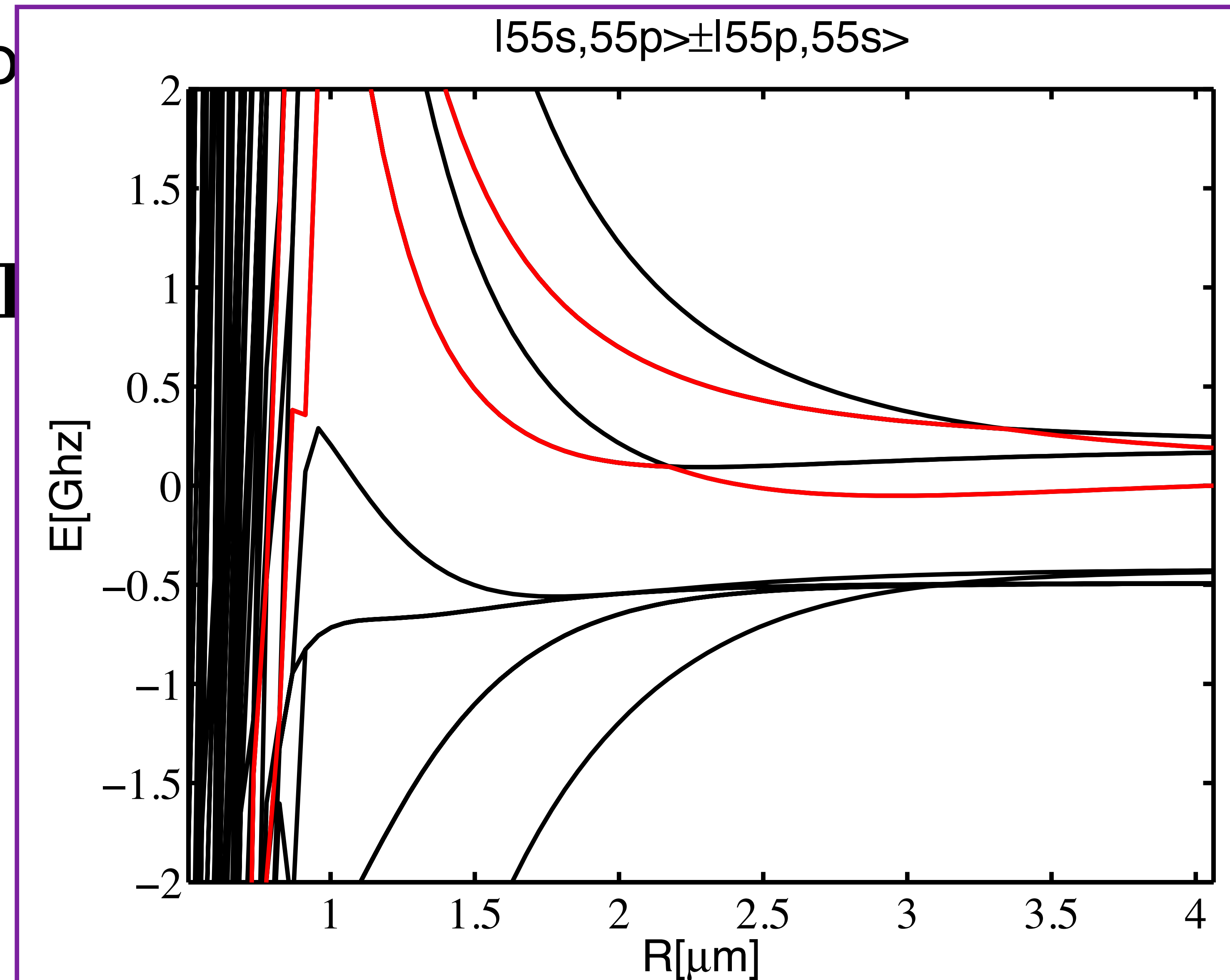
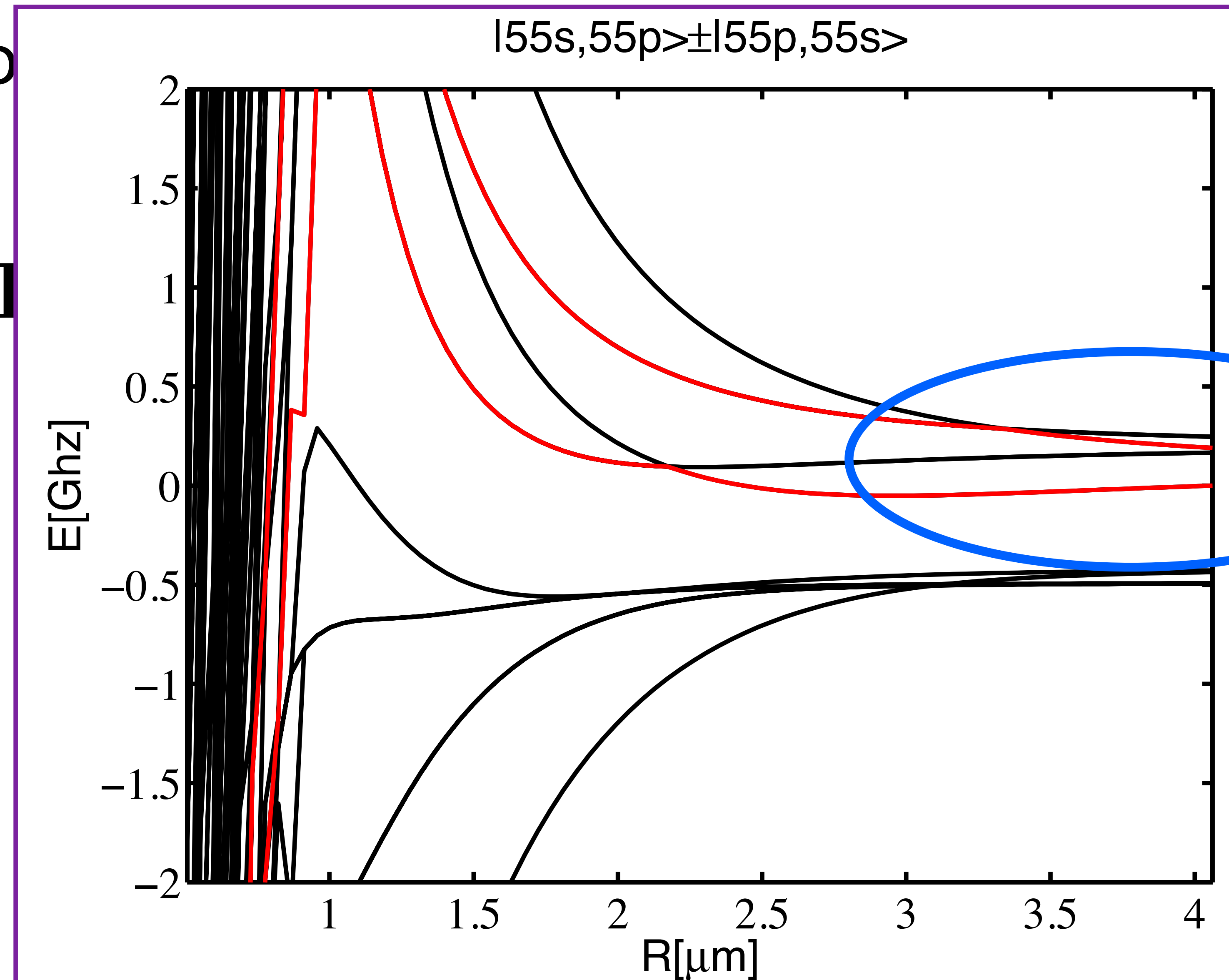


Rydberg interactions

Set up two-atom basis: $|\,\nu_1 j_1 m_1\,\rangle \otimes |\,\nu_2 j_2 m_2\,\rangle$

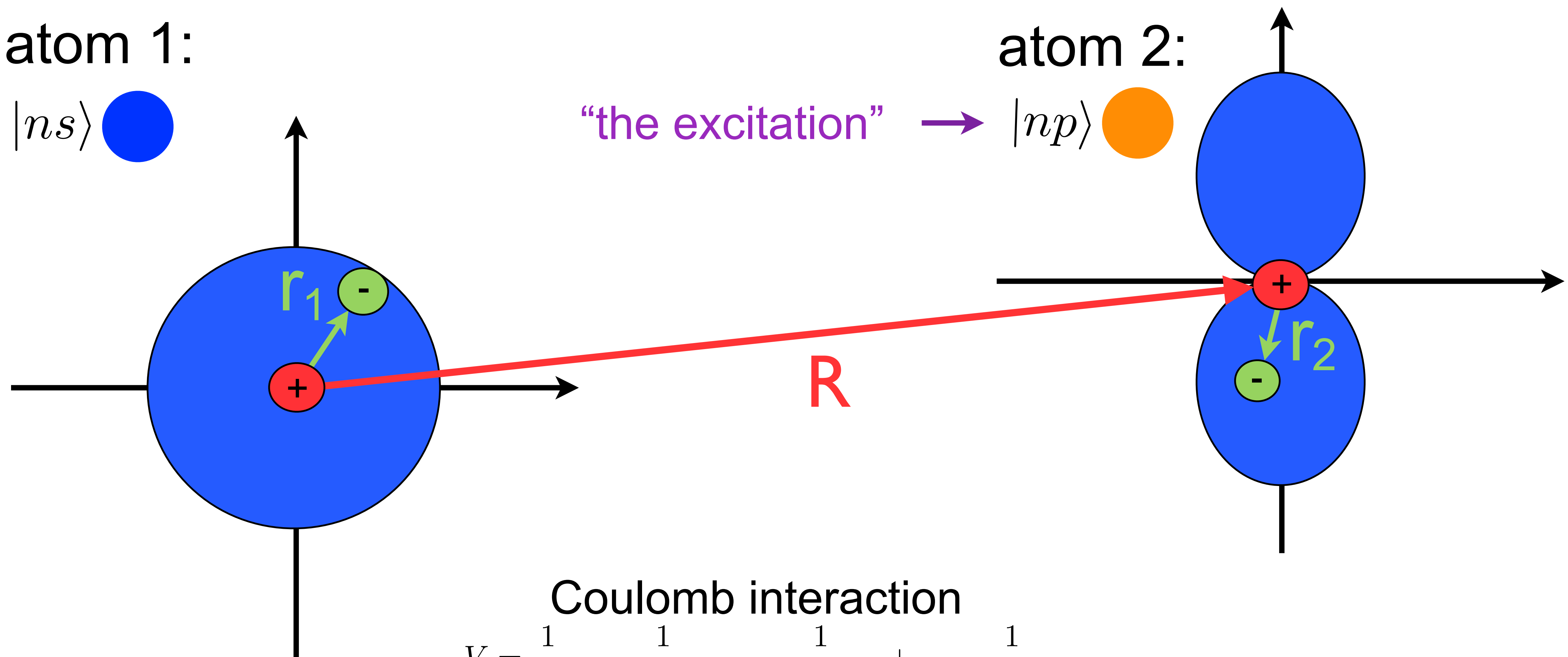
Determine interaction matrix elements (leading dipole-dipo

Diagonalize Hamiltonian $\hat{H}(\mathbf{I}$



Now: keep single atom state space simple, but move to more than two atoms

Resonant dipole-dipole interactions



Coulomb interaction

$$V = \frac{1}{\mathbf{R}} - \frac{1}{|\mathbf{R}+\mathbf{r}_2|} - \frac{1}{|\mathbf{R}-\mathbf{r}_1|} + \frac{1}{|\mathbf{R}+\mathbf{r}_2-\mathbf{r}_1|}$$
$$= \frac{\mathbf{r}_1\cdot\mathbf{r}_2 - 3(\mathbf{r}_1\cdot\hat{\mathbf{R}})(\mathbf{r}_2\cdot\hat{\mathbf{R}})}{R^3}$$

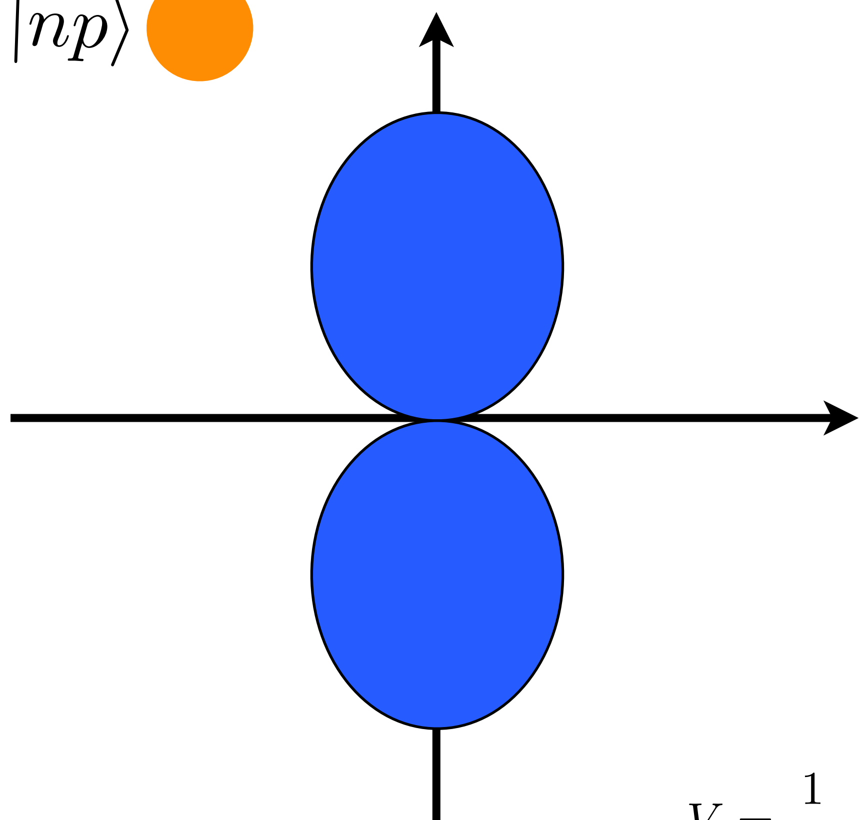
Excitation transfer

$$\langle ns|\langle np|V|np\rangle|ns\rangle \neq 0$$

Resonant dipole-dipole interactions

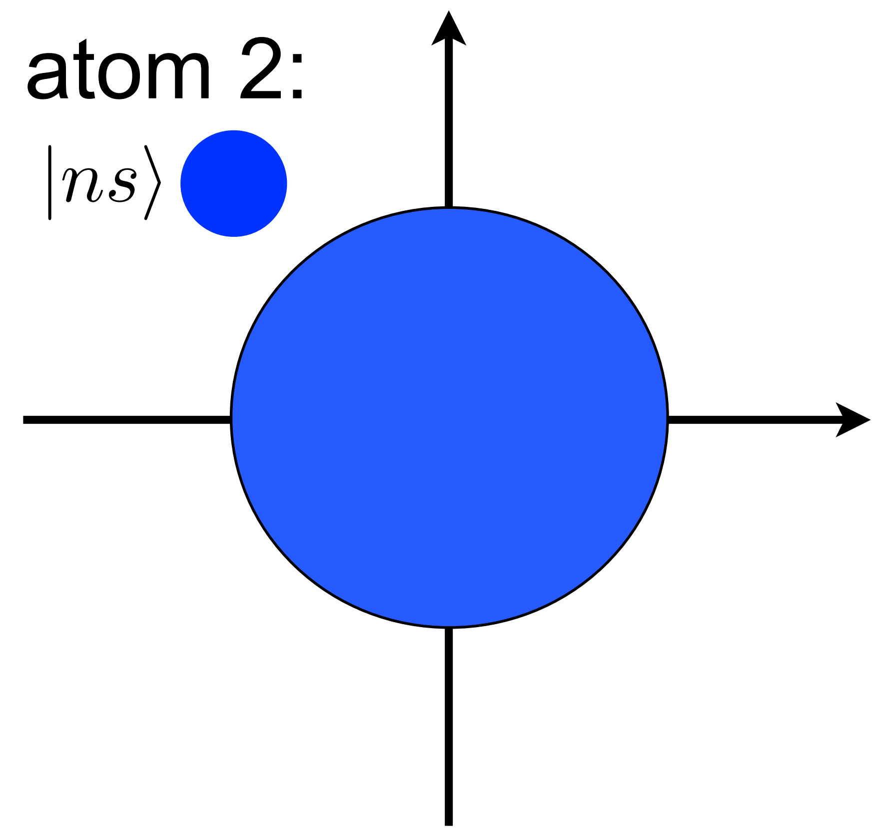
atom 1:

$|np\rangle$



atom 2:

$|ns\rangle$



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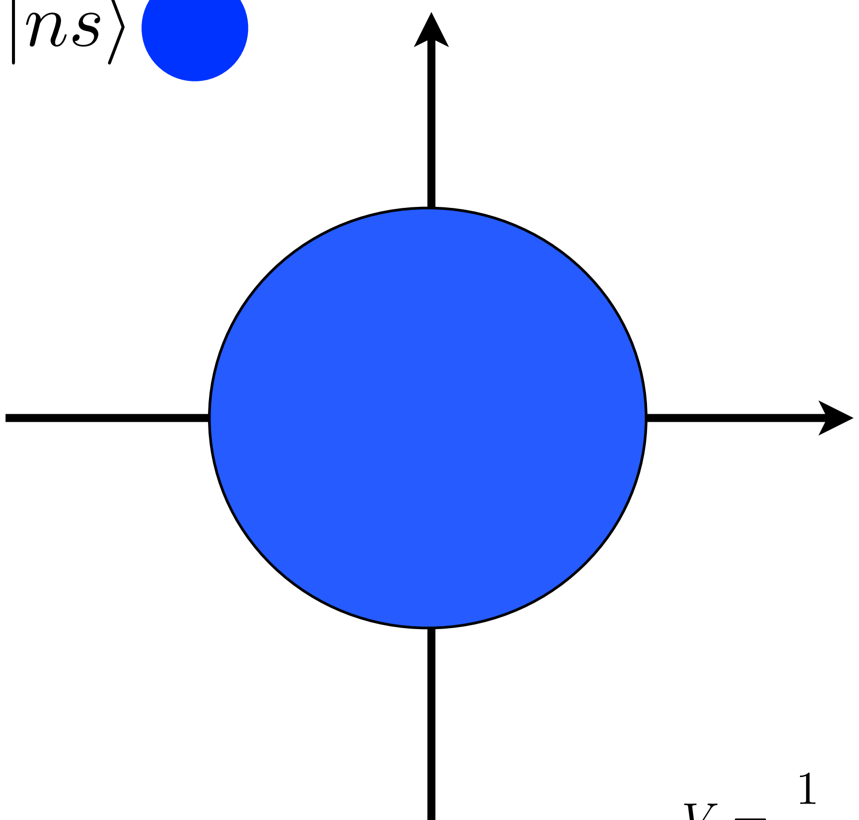

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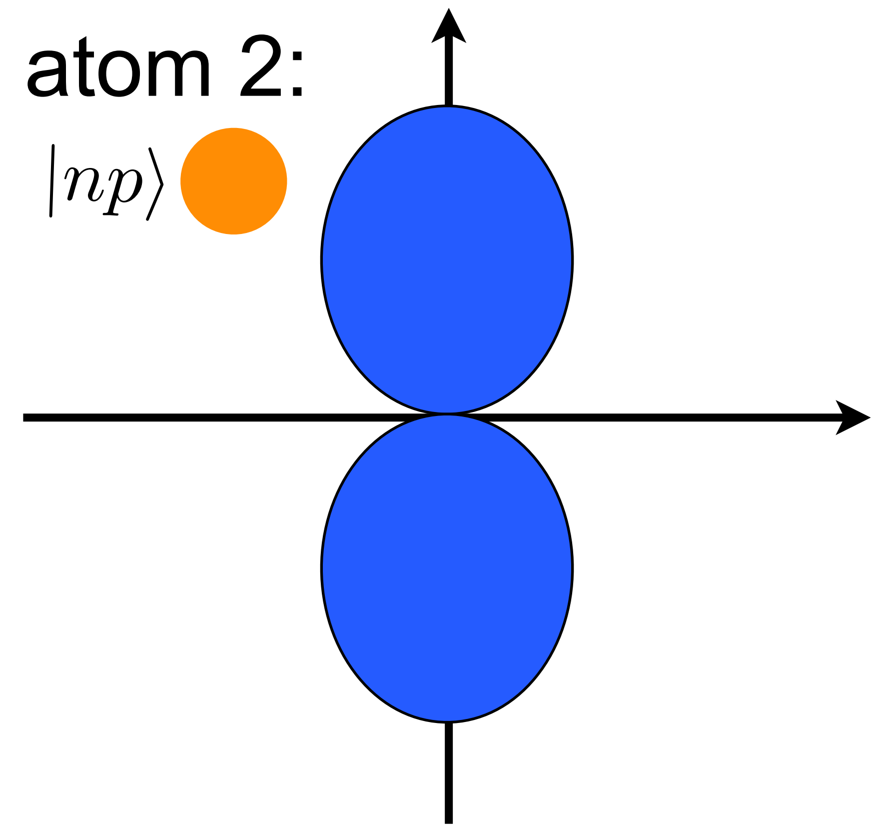

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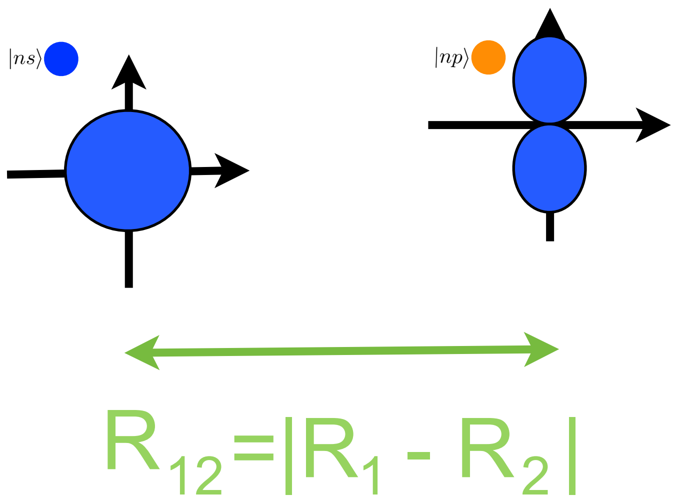
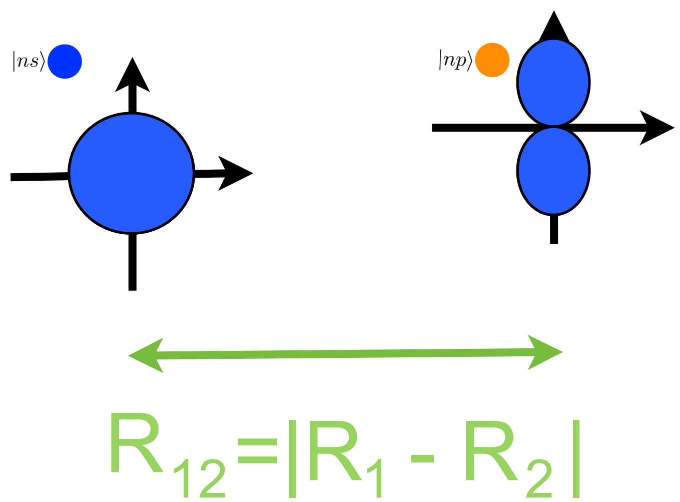
Motion from resonant dipole-dipole interactions



electronic dipole-dipole Hamiltonian:

$$\begin{array}{cc} & \begin{array}{cc} |\,ps\,\rangle & |\,sp\,\rangle \end{array} \\ H_{el} = -\mu^2 & \left(\begin{array}{cc} 0 & \frac{1}{R_{12}^3} \\ \frac{1}{R_{21}^3} & 0 \end{array} \right) \end{array}$$

Motion from resonant dipole-dipole interactions



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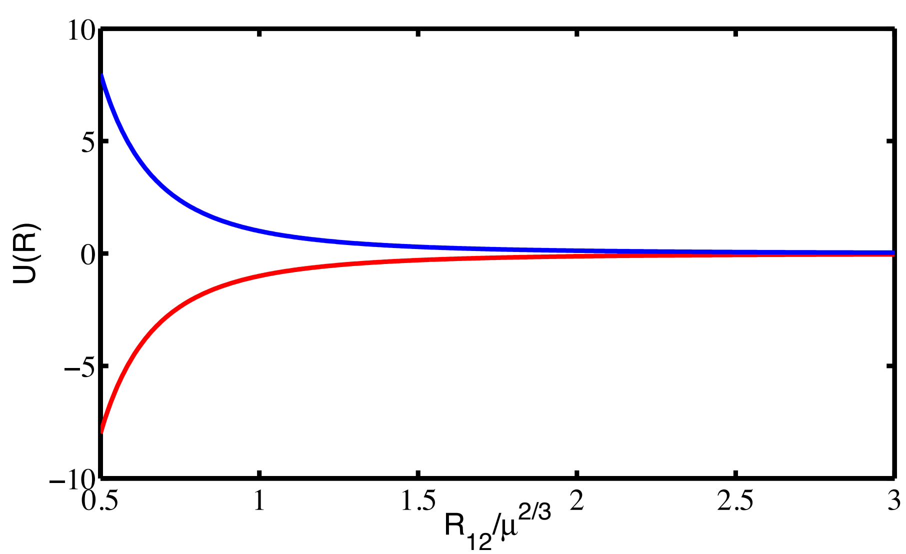

“attractive” eigenstate (exciton)

$$|\varphi_1\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle + |ps\rangle\right) \qquad U_1 = -\frac{\mu^2}{R_{12}^3}$$

“repulsive” eigenstate (exciton)

$$|\varphi_2\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle - |ps\rangle\right) \qquad U_2 = +\frac{\mu^2}{R_{12}^3}$$

Molecular physics perspective

- Coordinates *electrons:* $\mathbf{r} = (r_1, r_2, \cdots r_N)$

  nucleii: $\mathbf{R} = (R_1, R_2, \cdots R_N)$

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$$\hat{H}_{nuc} = -\sum_n \frac{\hbar^2 \nabla_R^2}{2M} + \frac{1}{2}\sum_{n\neq m} \frac{z_n z_m e^2}{|R_n - R_m|}$$
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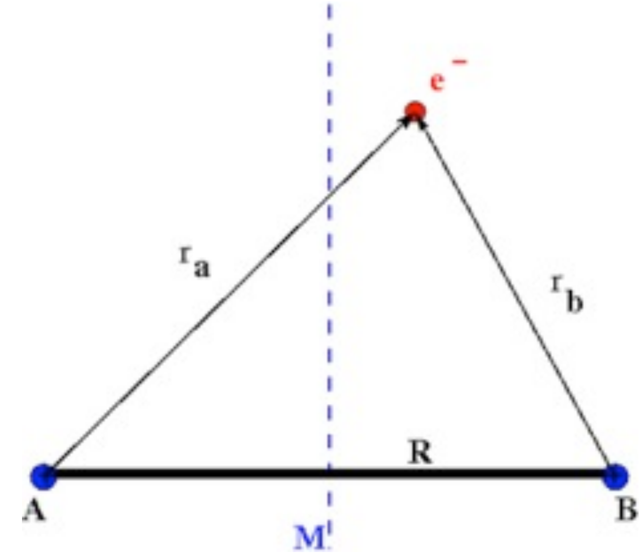

- Electronic eigenstates $\hat{H}_{el}(\mathbf{R})|\varphi_k(\mathbf{r},\mathbf{R})\rangle = U_k(\mathbf{R})|\varphi_k(\mathbf{r},\mathbf{R})\rangle$
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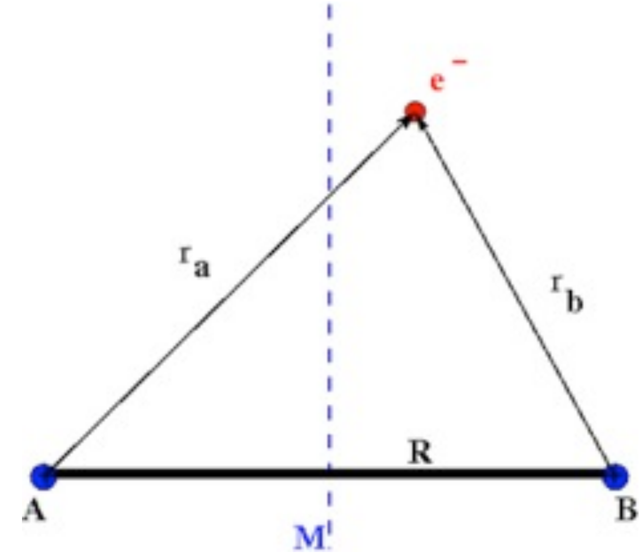
$$i\hbar\frac{\partial}{\partial t}\phi_k(\mathbf{R}) = \left(\sum_n -\frac{\hbar^2}{2M}\nabla_{R_n}^2 + U_k(\mathbf{R})\right)\phi_k(\mathbf{R}) + \sum_{m\neq k}\theta_{km}(\mathbf{R})\phi_m(\mathbf{R})$$

Molecular physics perspective



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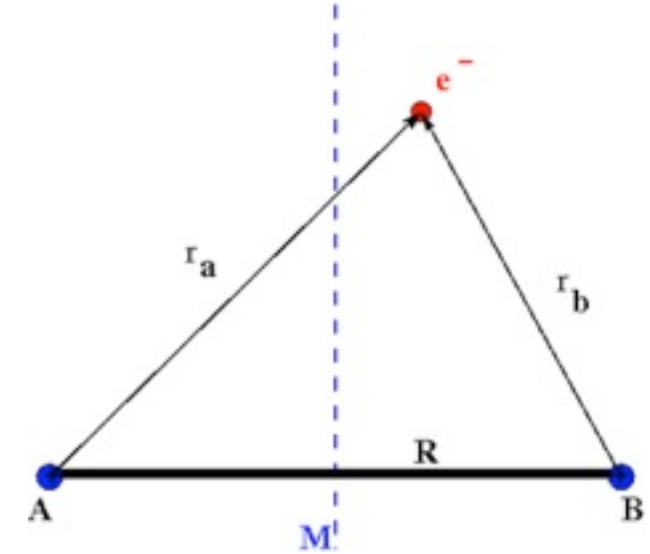
Molecular physics perspective



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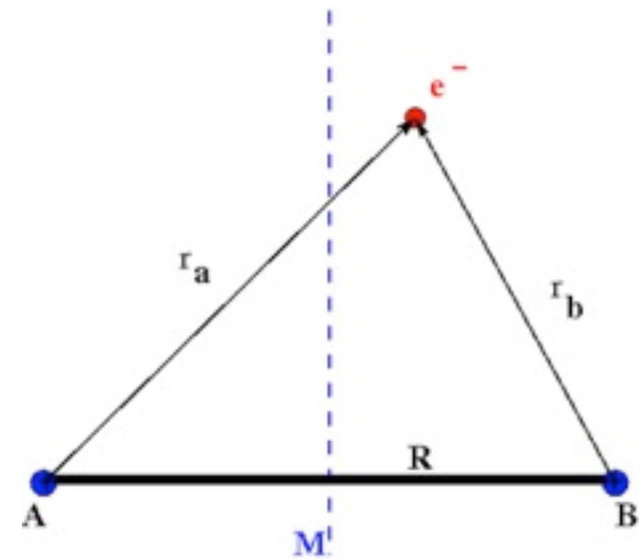
Molecular physics perspective



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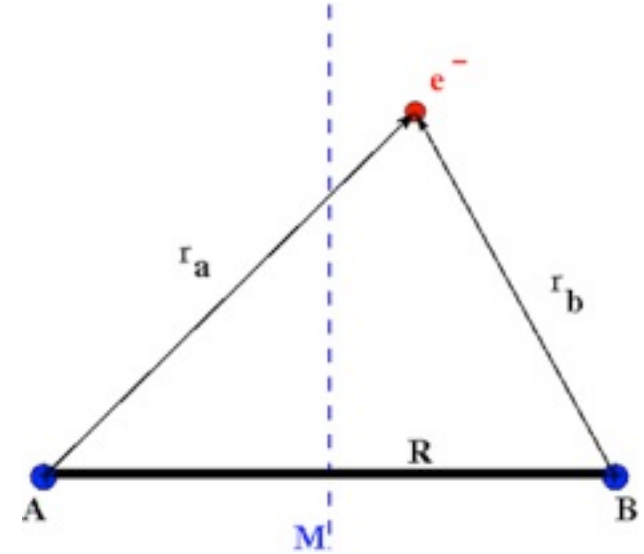

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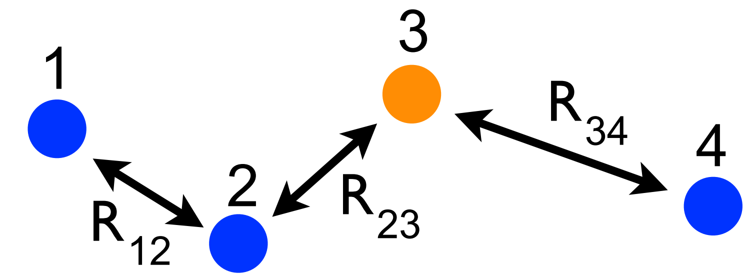
- Born-Oppenheimer *Approximation*

Excitonic Born-Oppenheimer surfaces



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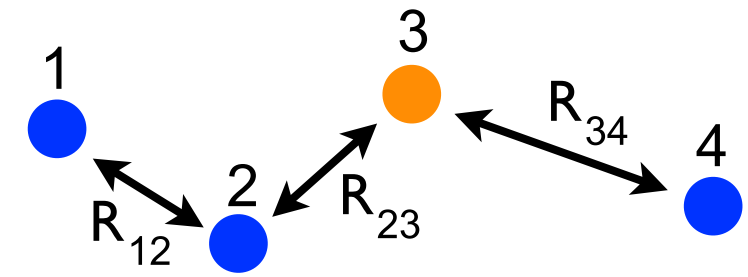

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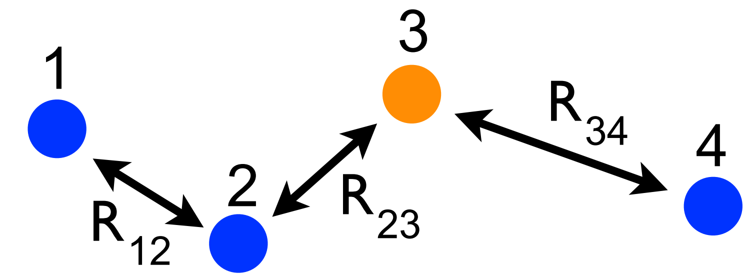
Excitonic Born-Oppenheimer surfaces



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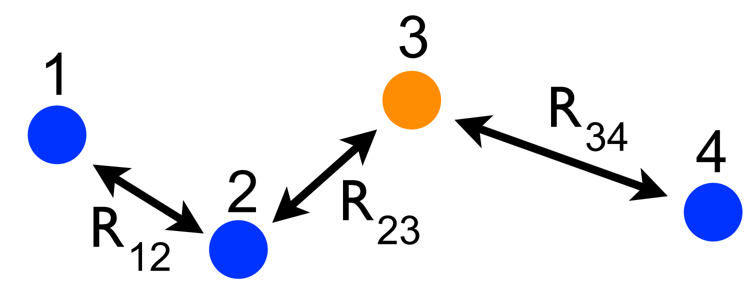
Excitonic Born-Oppenheimer surfaces



- Coordinates

  electrons: $| \, s \, \bullet \, \rangle \quad | \, p \, \bullet \, \rangle$

  nucleii: $\mathbf{R} = (R_1, R_2, \cdots R_N)$

- Hamiltonian

$$\hat{H}_{nuc} = -\sum_n \frac{\hbar^2 \nabla_R^2}{2M}$$

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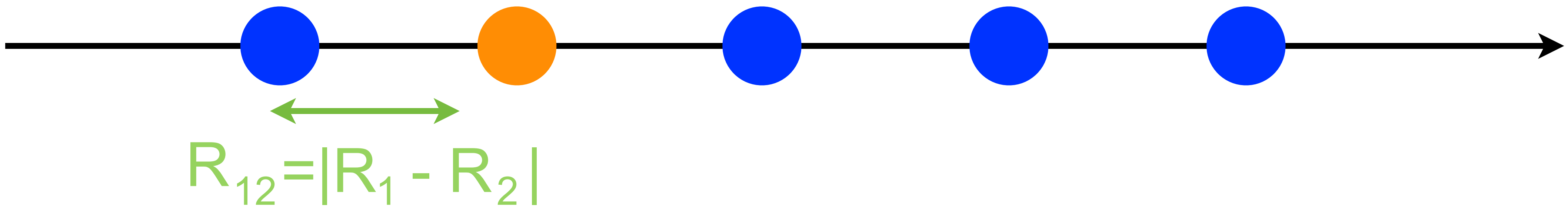
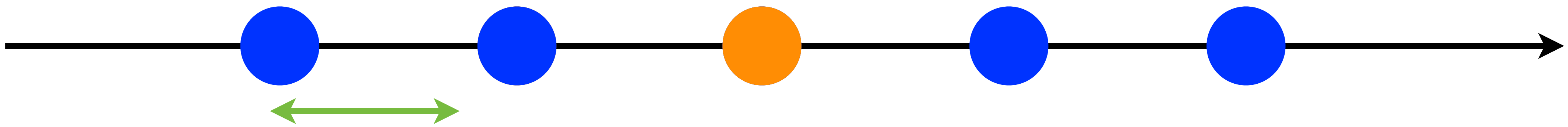
Motion depends on quantum state



$$|\pi_2\rangle = |spsss\rangle$$

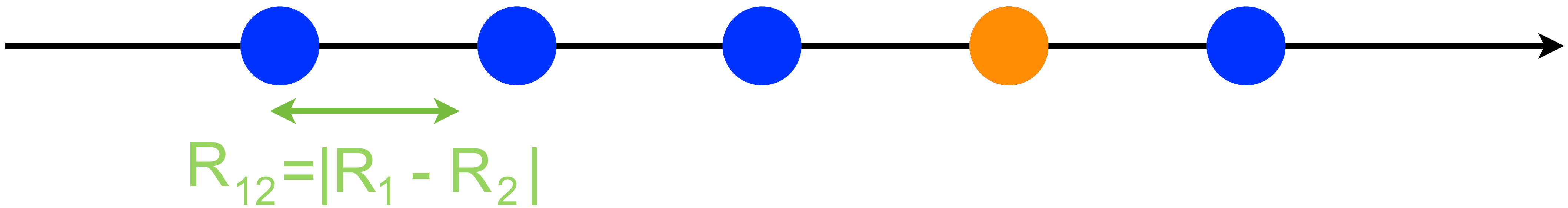
Motion depends on quantum state



$R_{12}=|R_1 - R_2|$

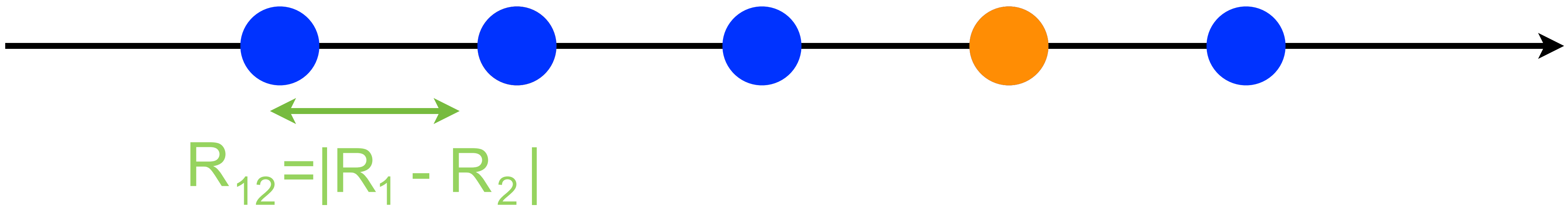
$$|\pi_3\rangle = |sspss\rangle$$

Motion depends on quantum state



$$|\pi_4\rangle = |sssps\rangle$$

Motion depends on quantum state

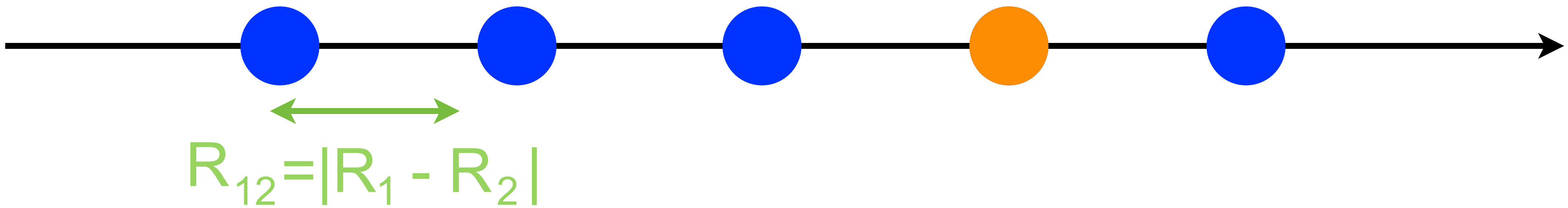


$$|\pi_4\rangle = |sssps\rangle$$

electronic dipole-dipole
Hamiltonian:

$$H_{el} = -\mu^2 \begin{pmatrix} 0 & \frac{1}{R_{12}^3} & \frac{1}{R_{13}^3} & \frac{1}{R_{14}^3} & \frac{1}{R_{15}^3} \\ \frac{1}{R_{21}^3} & 0 & \frac{1}{R_{23}^3} & \frac{1}{R_{24}^3} & \frac{1}{R_{25}^3} \\ \frac{1}{R_{31}^3} & \frac{1}{R_{32}^3} & 0 & \frac{1}{R_{34}^3} & \frac{1}{R_{35}^3} \\ \frac{1}{R_{41}^3} & \frac{1}{R_{42}^3} & \frac{1}{R_{43}^3} & 0 & \frac{1}{R_{45}^3} \\ \frac{1}{R_{51}^3} & \frac{1}{R_{52}^3} & \frac{1}{R_{53}^3} & \frac{1}{R_{54}^3} & 0 \end{pmatrix}$$

Motion depends on quantum state



$$|\pi_4\rangle = |sssps\rangle$$

electronic dipole-dipole Hamiltonian:

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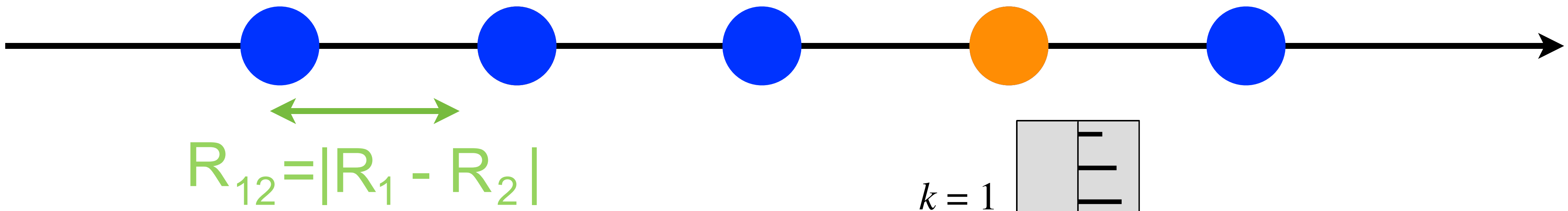
$$H^{\text{el}}(\mathbf{R})|\,\varphi_n(\mathbf{R})\,\rangle = U_n(\mathbf{R})|\,\varphi_n(\mathbf{R})\,\rangle$$

$$|\varphi_n(\mathbf{R})\rangle = \sum_m c_{nm}(\mathbf{R})|\,\pi_m\,\rangle$$

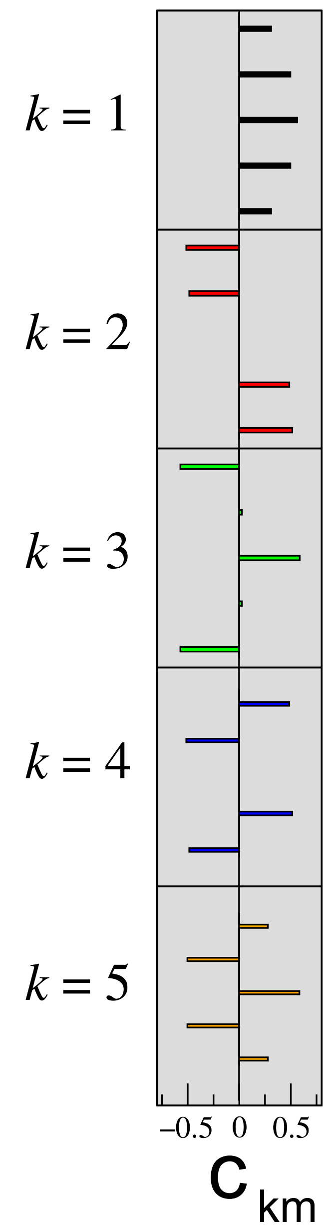
Motion depends on quantum state



$$|\pi_4\rangle = |sssps\rangle$$

electronic dipole-dipole Hamiltonian:

$$H_{el} = -\mu^2 \begin{pmatrix} 0 & \frac{1}{R_{12}^3} & \frac{1}{R_{13}^3} & \frac{1}{R_{14}^3} & \frac{1}{R_{15}^3} \\ \frac{1}{R_{21}^3} & 0 & \frac{1}{R_{23}^3} & \frac{1}{R_{24}^3} & \frac{1}{R_{25}^3} \\ \frac{1}{R_{31}^3} & \frac{1}{R_{32}^3} & 0 & \frac{1}{R_{34}^3} & \frac{1}{R_{35}^3} \\ \frac{1}{R_{41}^3} & \frac{1}{R_{42}^3} & \frac{1}{R_{43}^3} & 0 & \frac{1}{R_{45}^3} \\ \frac{1}{R_{51}^3} & \frac{1}{R_{52}^3} & \frac{1}{R_{53}^3} & \frac{1}{R_{54}^3} & 0 \end{pmatrix}$$

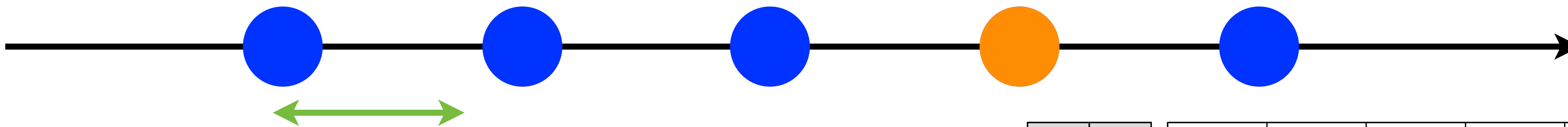


$$H^{\mathrm{el}}(\mathbf{R})|\,\varphi_n(\mathbf{R})\,\rangle = U_n(\mathbf{R})|\,\varphi_n(\mathbf{R})\,\rangle$$

$$|\varphi_n(\mathbf{R})\rangle = \sum_m c_{nm}(\mathbf{R})|\,\pi_m\,\rangle$$

C. Ates, A. Eisfeld, J.-M. Rost
New J. Phys., **10** 045030 (2008).

Motion depends on quantum state



$R_{12}=|R_1 - R_2|$

$$|\pi_4\rangle = |sssps\rangle$$

electronic dipole-dipole Hamiltonian:

$$H_{el} = -\mu^2 \begin{pmatrix} 0 & \frac{1}{R_{12}^3} & \frac{1}{R_{13}^3} & \frac{1}{R_{14}^3} & \frac{1}{R_{15}^3} \\ \frac{1}{R_{21}^3} & 0 & \frac{1}{R_{23}^3} & \frac{1}{R_{24}^3} & \frac{1}{R_{25}^3} \\ \frac{1}{R_{31}^3} & \frac{1}{R_{32}^3} & 0 & \frac{1}{R_{34}^3} & \frac{1}{R_{35}^3} \\ \frac{1}{R_{41}^3} & \frac{1}{R_{42}^3} & \frac{1}{R_{43}^3} & 0 & \frac{1}{R_{45}^3} \\ \frac{1}{R_{51}^3} & \frac{1}{R_{52}^3} & \frac{1}{R_{53}^3} & \frac{1}{R_{54}^3} & 0 \end{pmatrix}$$

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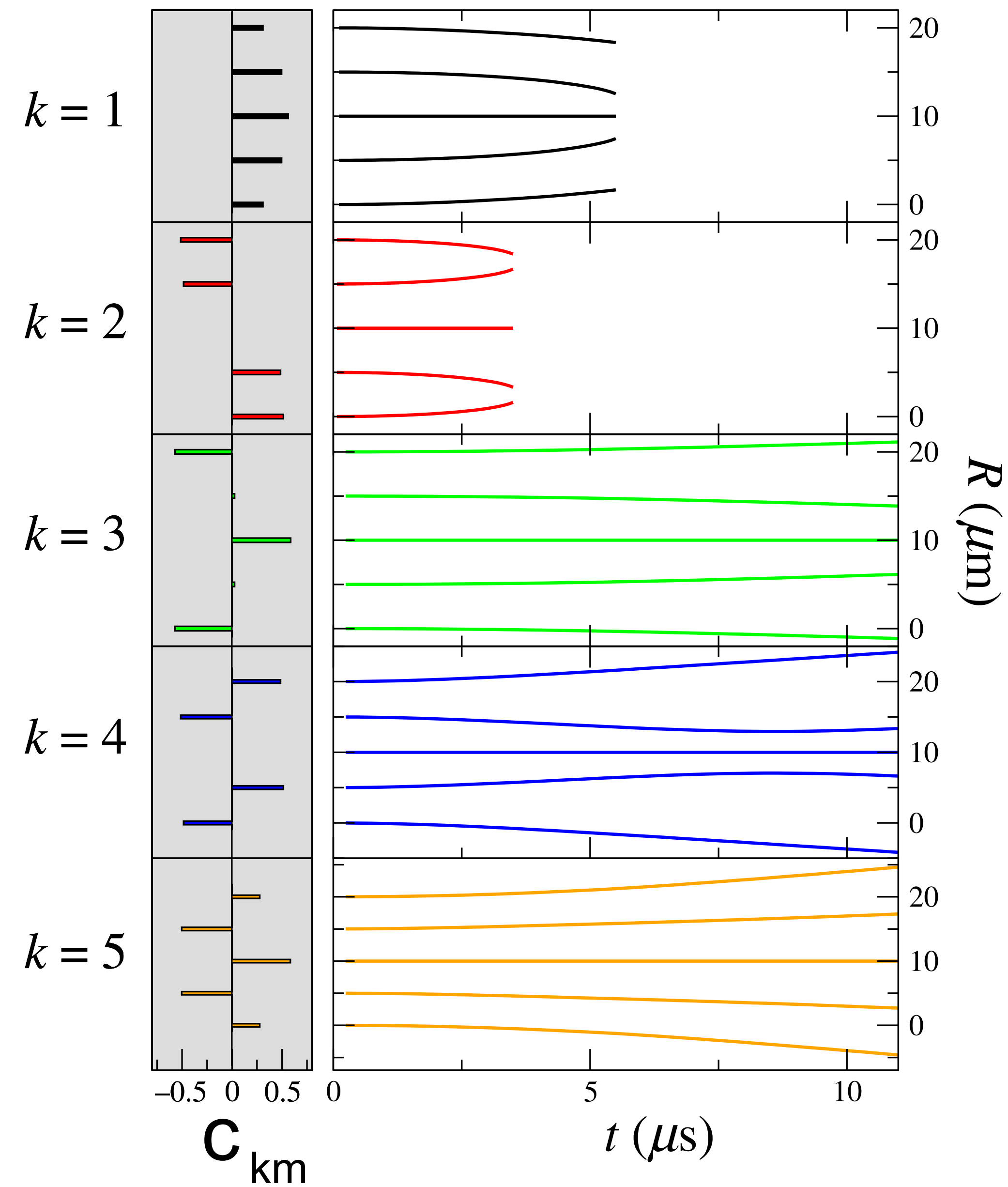
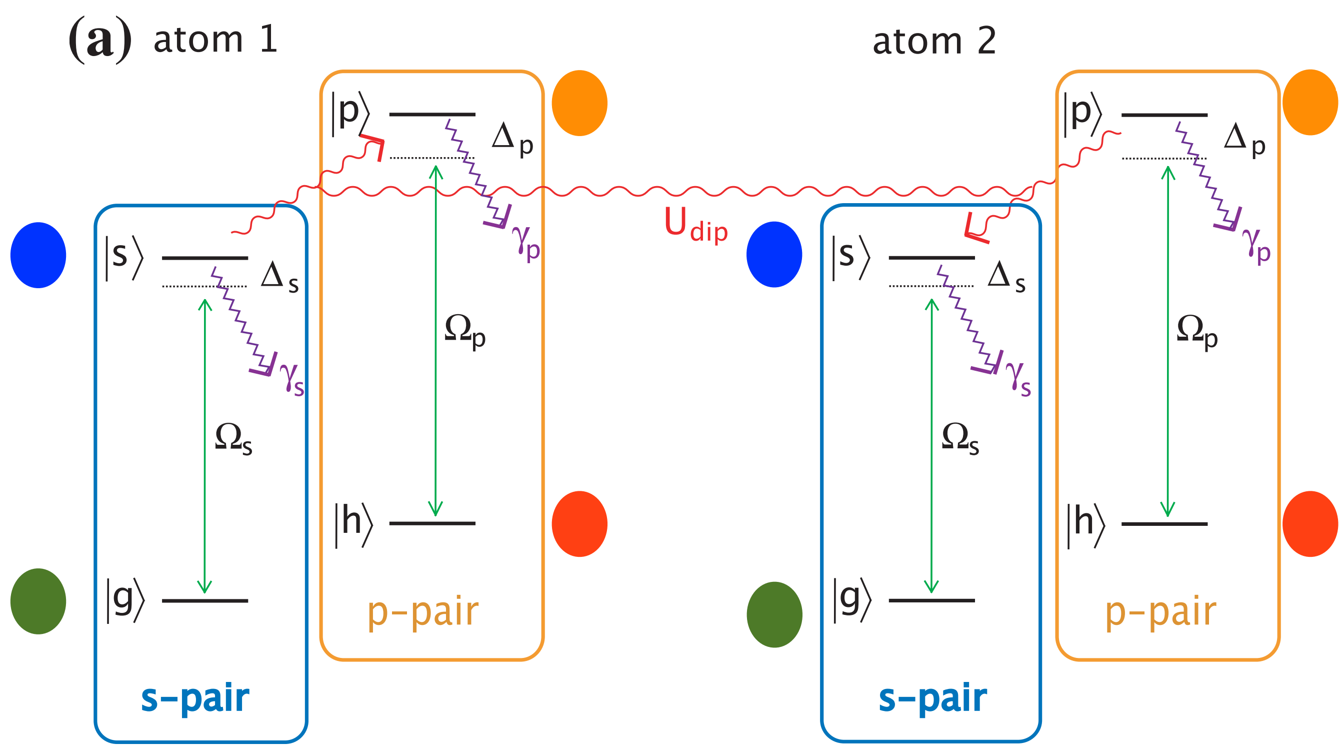
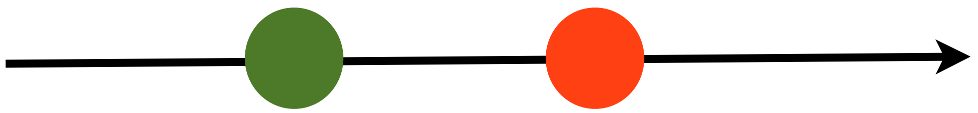


C. Ates, A. Eisfeld, J.-M. Rost
New J. Phys., **10** 045030 (2008).

Rydberg dressed dipole-dipole interactions



*S. Wüster, C. Ates, A. Eisfeld and J. M. Rost, New J. Phys. **13** 073044 (2011).*



*adaptation of: M. Müller, L. Liang, I. Lesanovsky, P. Zoller, New J. Phys. , **10** 093009 (2008).*

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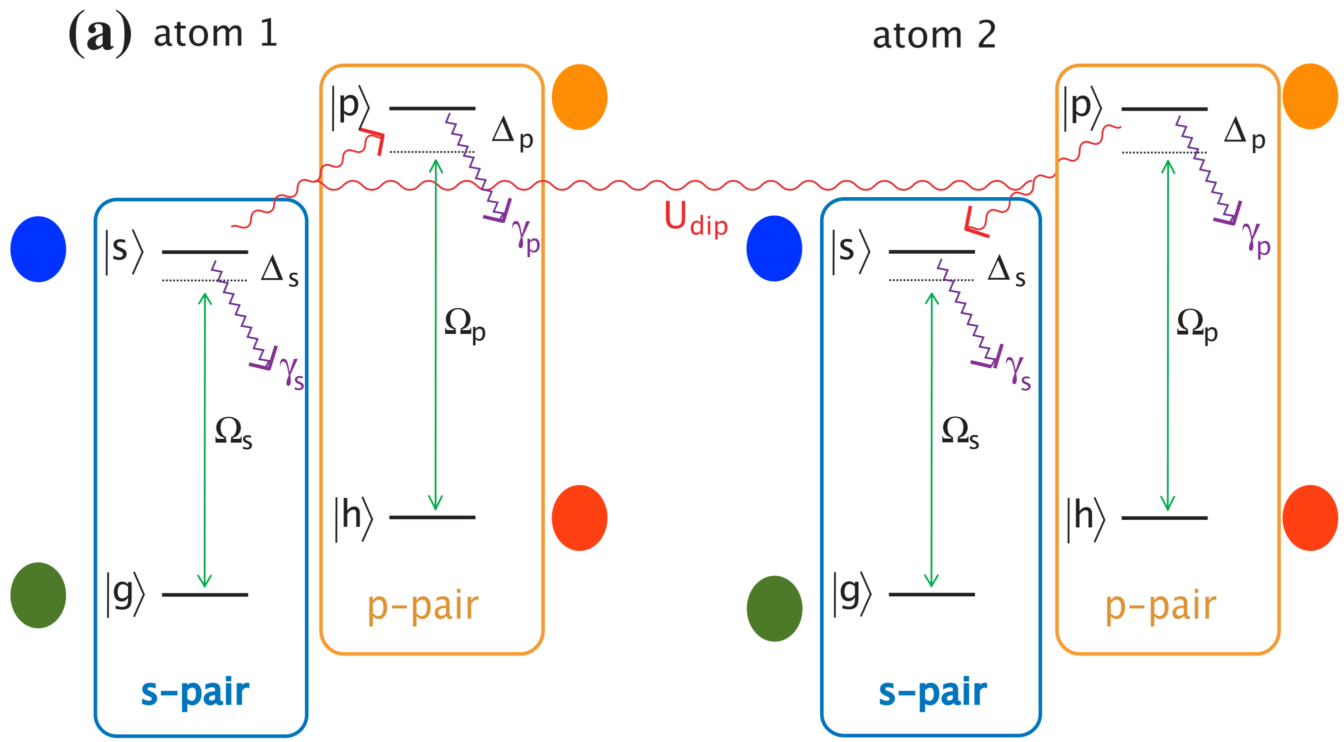

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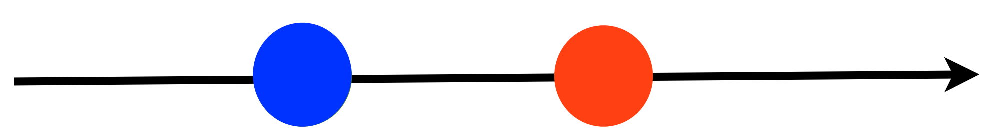

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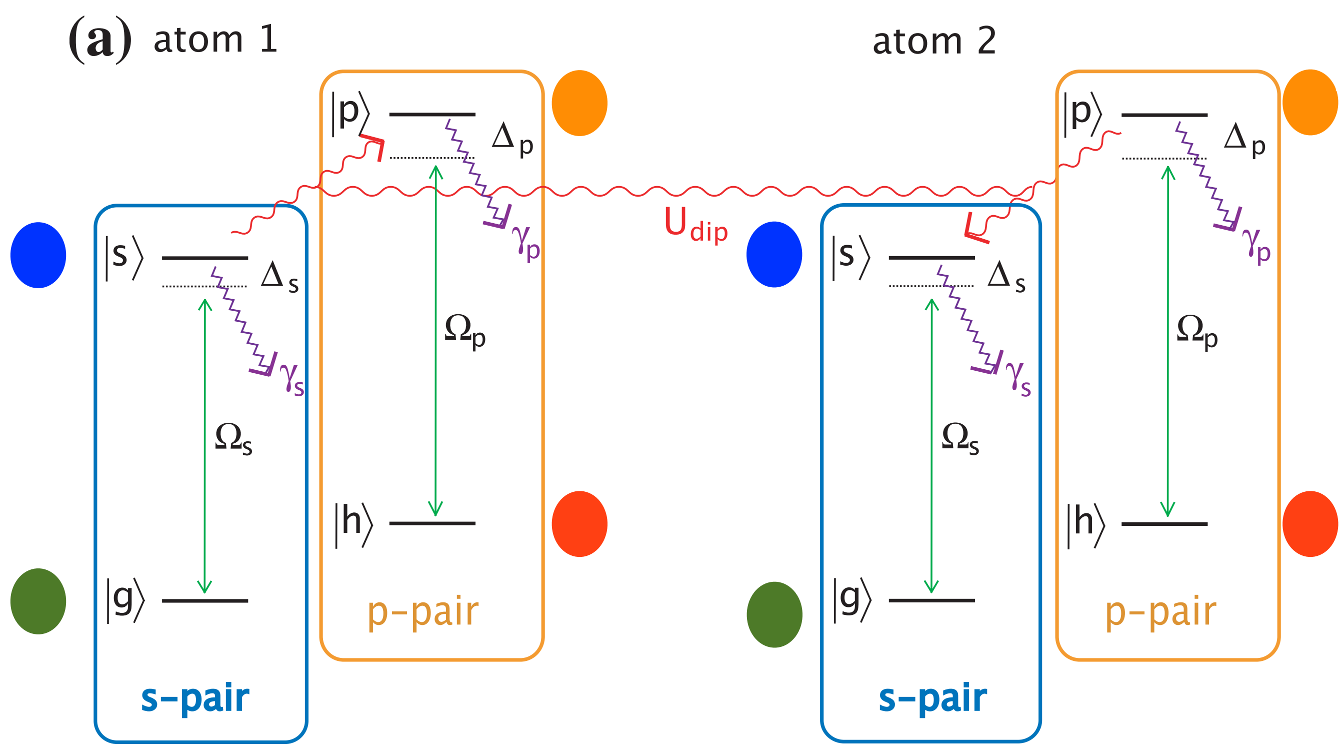

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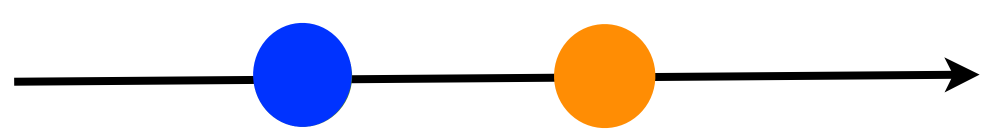

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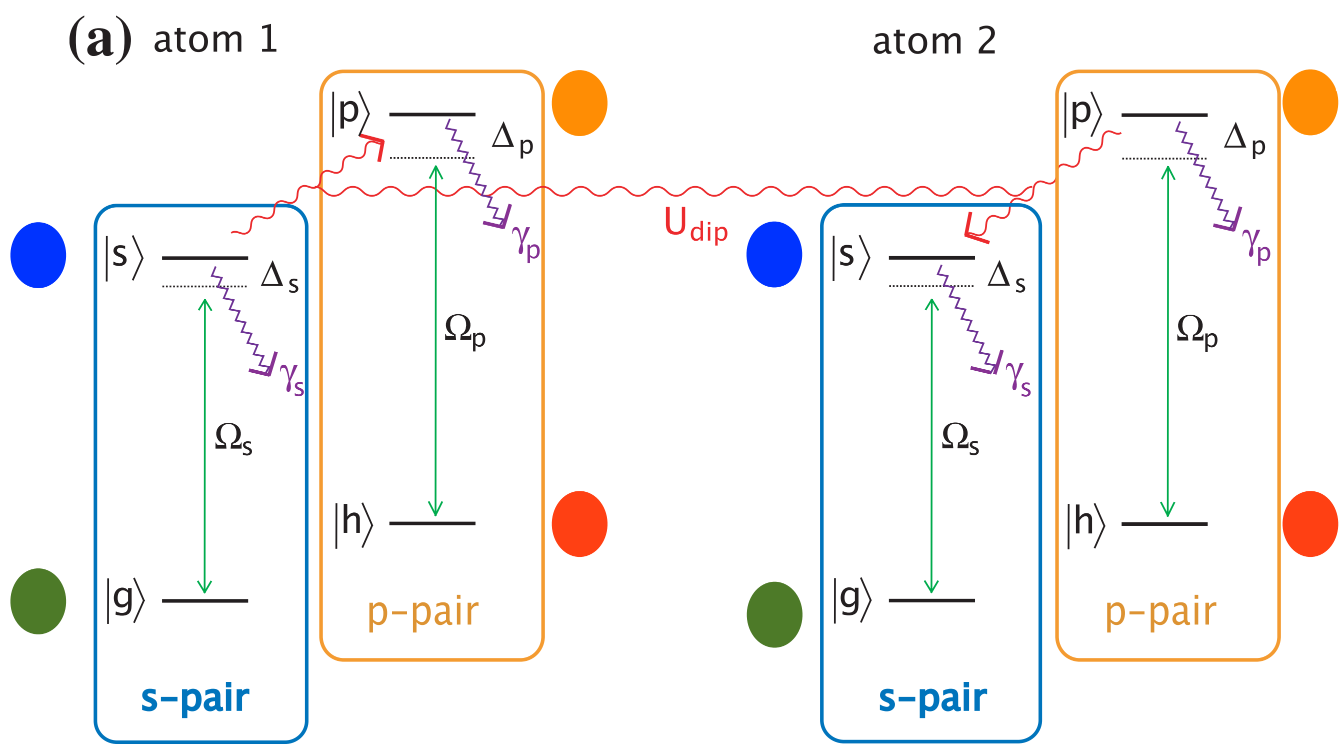

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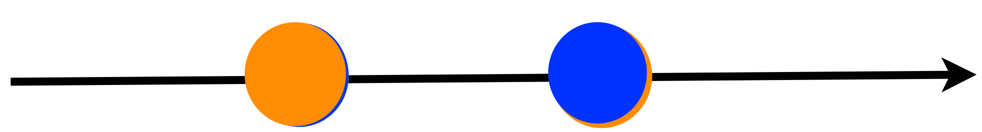

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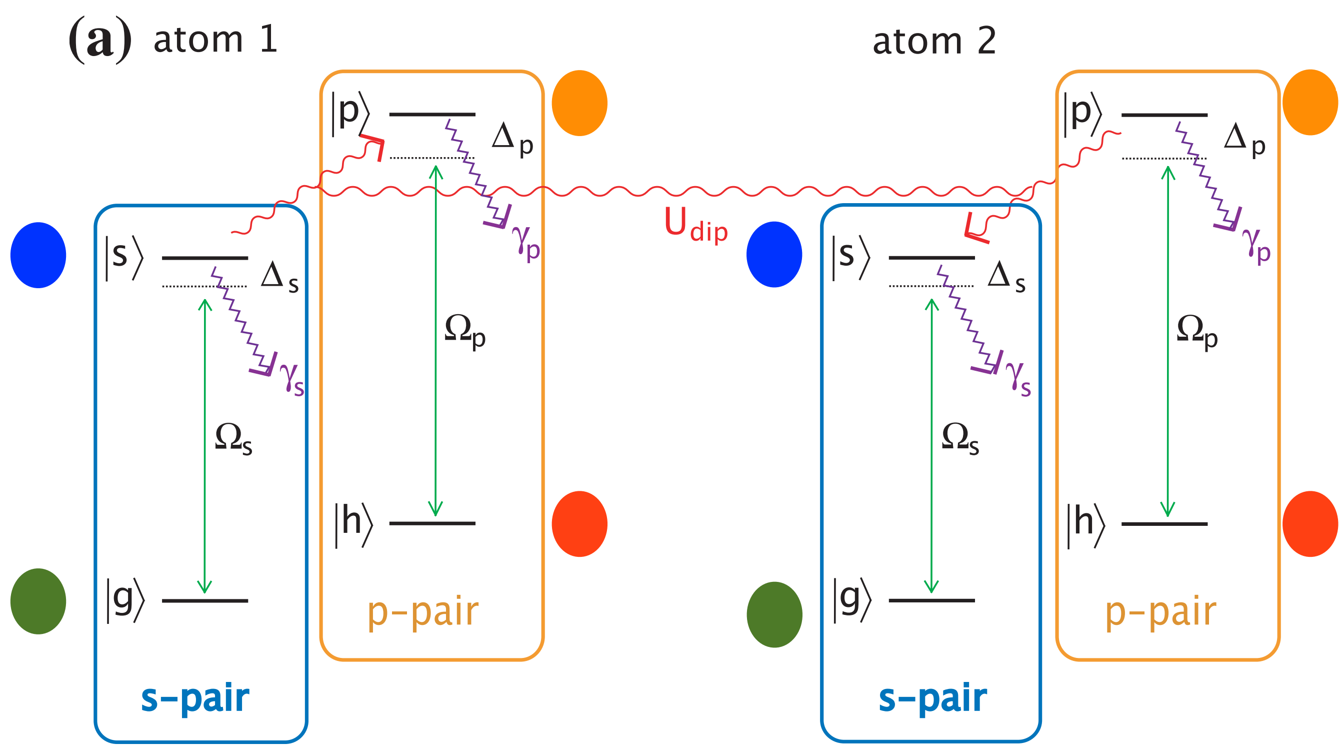

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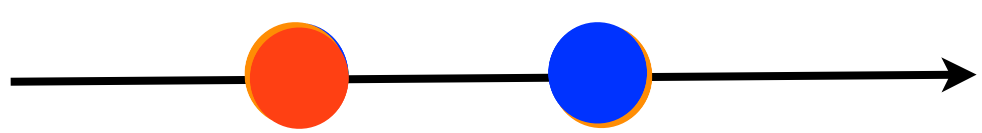

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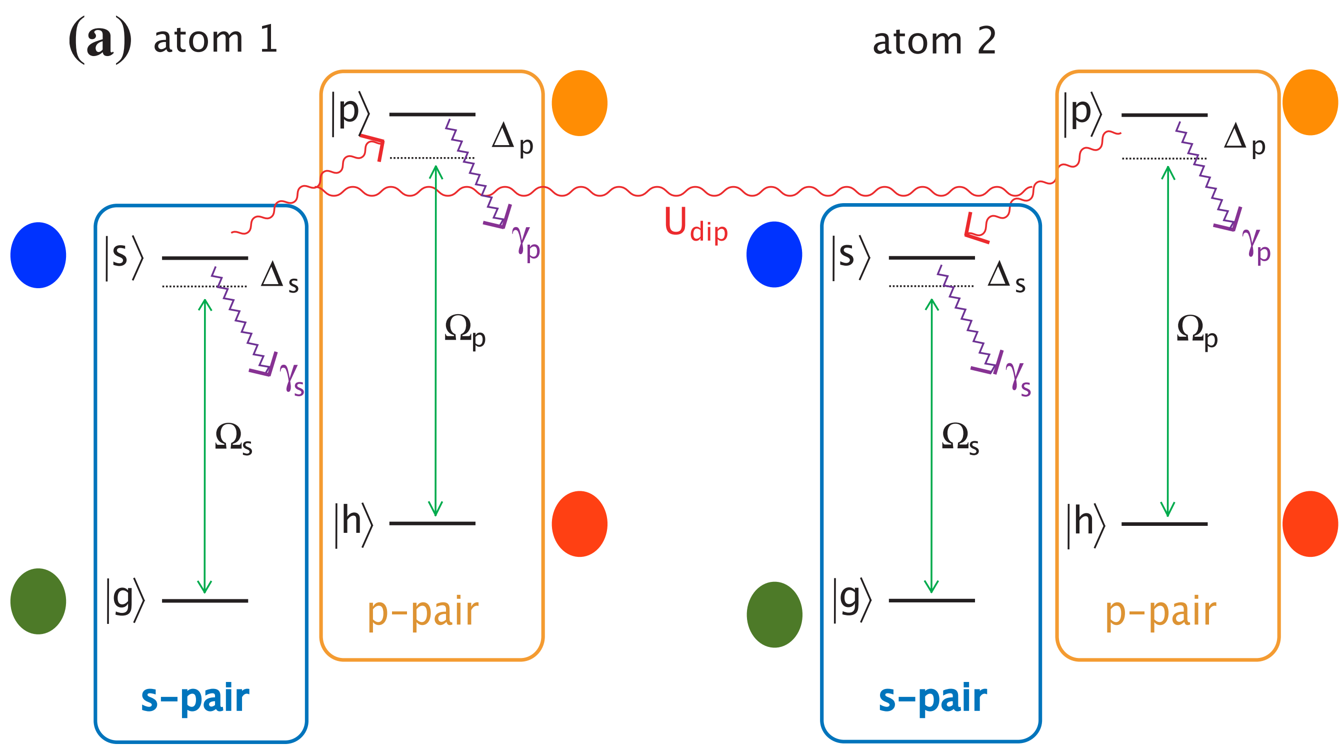

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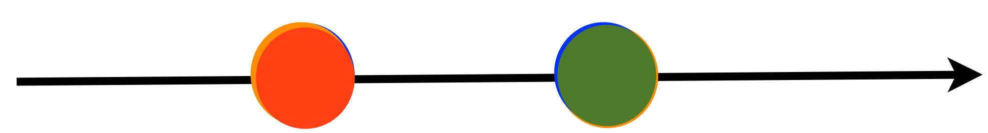

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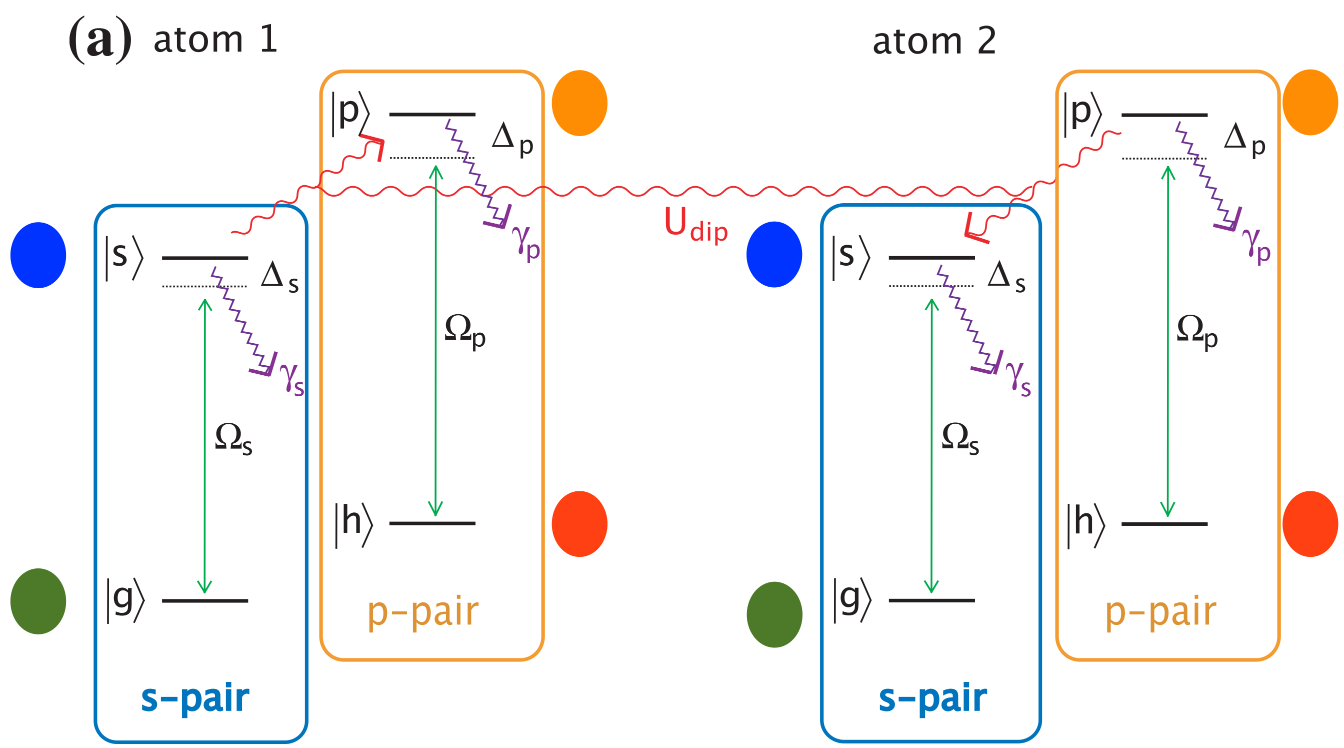

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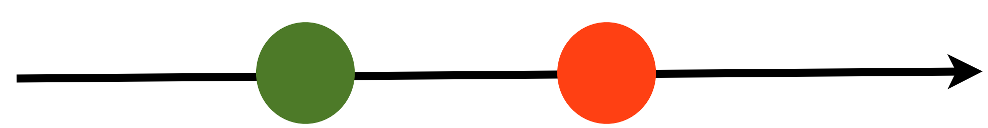

$$\hat{H}+ = V_{\rm eff}(|hg\rangle\langle gh| + |gh\rangle\langle hg|)$$

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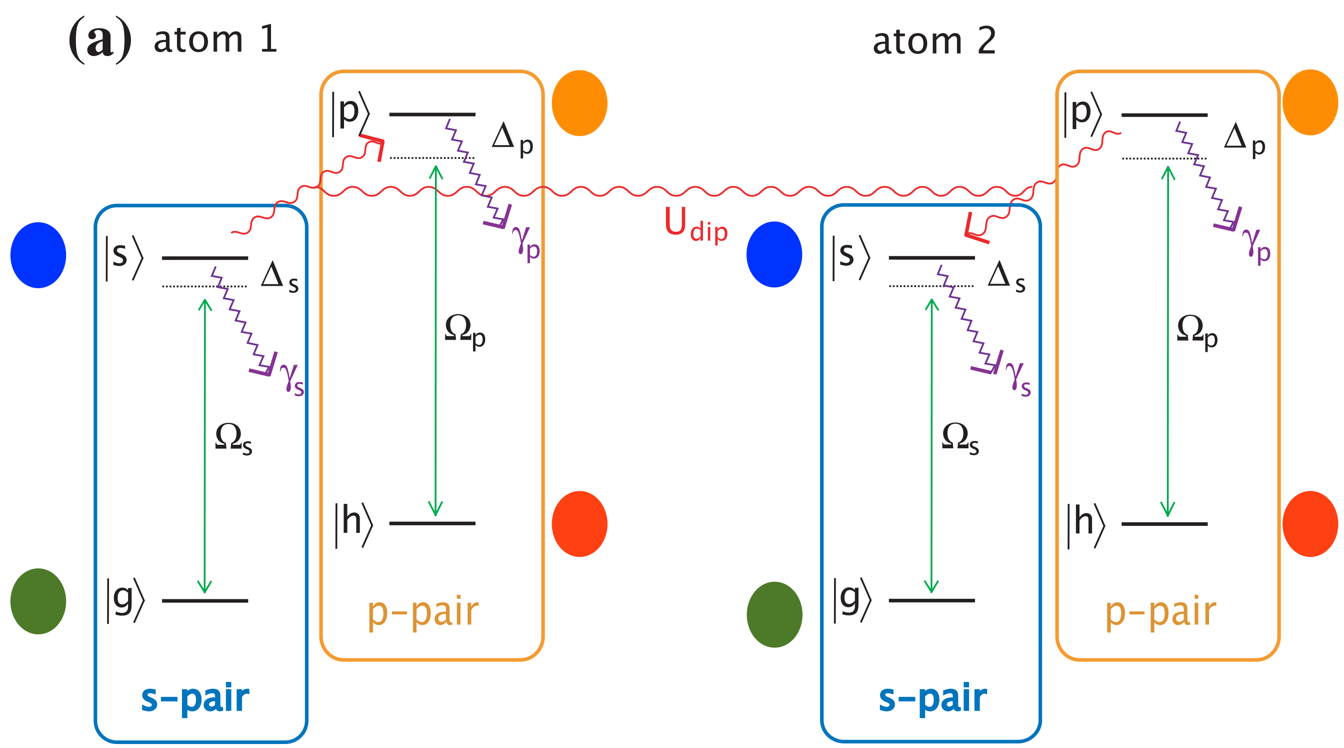
Rydberg dressed dipole-dipole interactions



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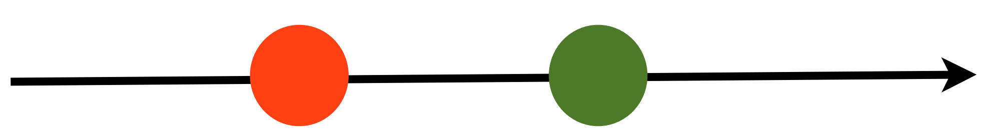

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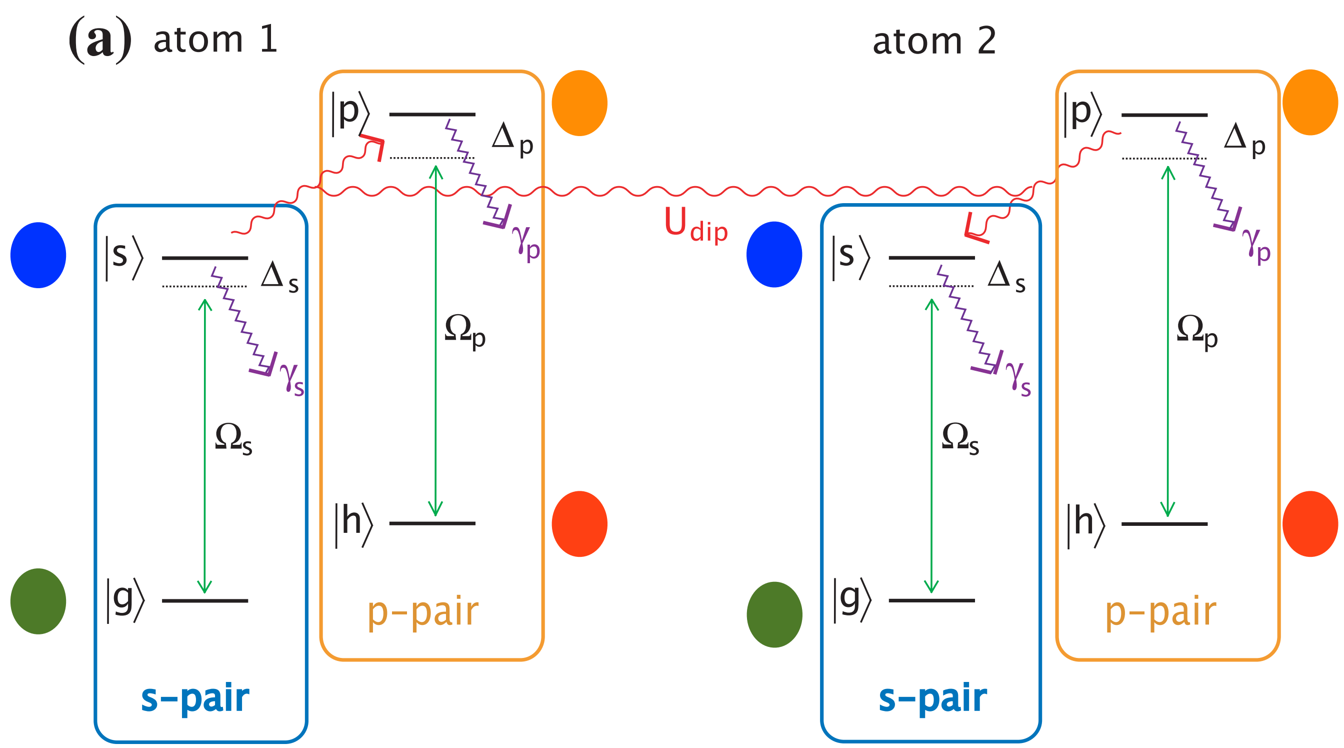
Rydberg dressed dipole-dipole interactions



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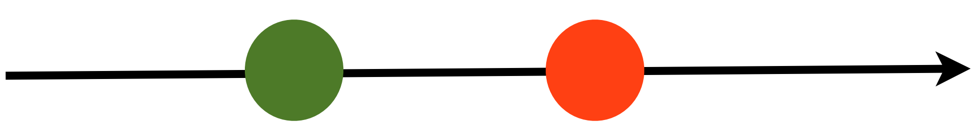

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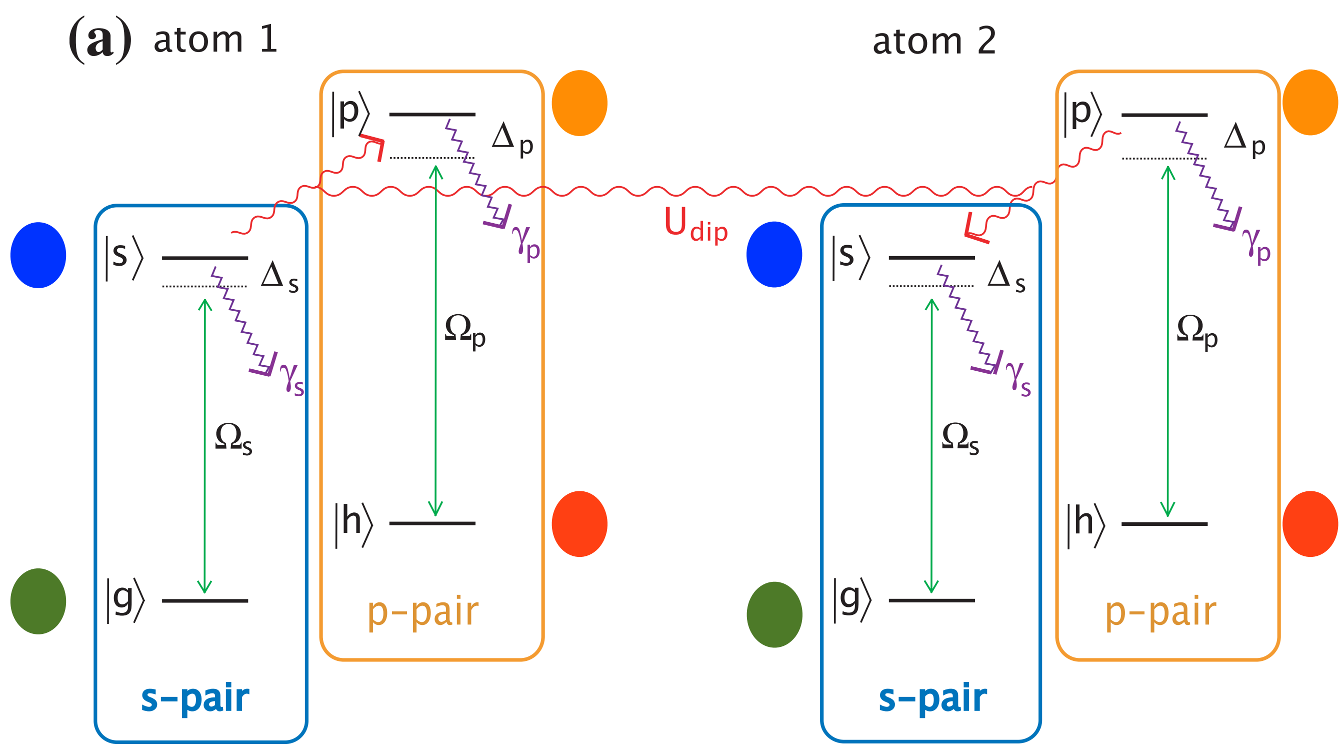

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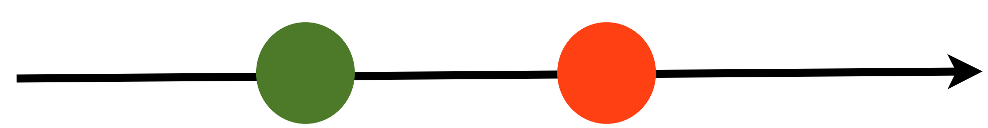


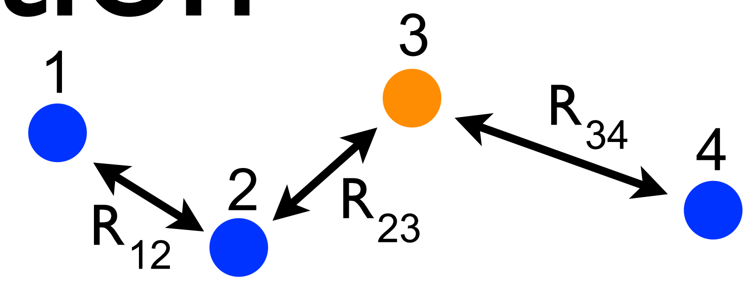
$$V_{\text{eff}} = \alpha_{\text{dress}}^4 V_{\text{dip-dip}}$$

$$\alpha_{\text{dress}} = \frac{\Omega}{2\Delta}$$

$$\hat{H}+ = V_{\text{eff}}(|hg\rangle\langle gh| + |gh\rangle\langle hg|)$$

(3) Linked motion and quantum state dynamics

Schrödinger's equation



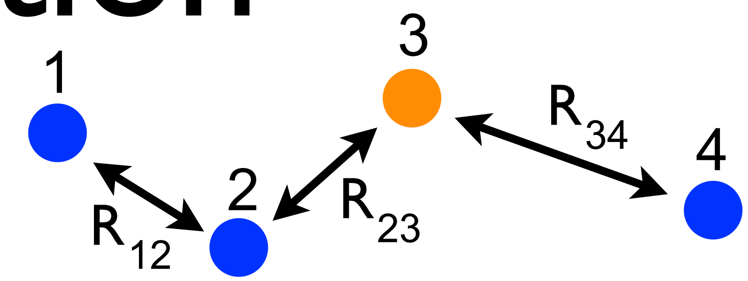
- Coordinates *electrons:* $|\, s \,\rangle$ $|\, p \,\rangle$
  nucleii: $\mathbf{R} = (R_1, R_2, \cdots R_N)$

- Hamiltonian
$$\hat{H}_{nuc} = -\sum_n \frac{\hbar^2 \nabla_R^2}{2M}$$
$$\hat{H}_{el} = -\sum_{nm} \frac{\mu^2}{|R_n - R_m|^3} |\, s_n p_m \,\rangle\langle\, p_n s_m \,| = \sum_{n,m} V(|R_n - R_m|) |\, \pi_n \,\rangle\langle\, \pi_m \,|$$

- Schrödinger's equation in the *adiabatic basis*
$$i\hbar \frac{\partial}{\partial t} \phi_k(\mathbf{R}) = \left(\sum_n -\frac{\hbar^2}{2M} \nabla_{R_n}^2 + U_k(\mathbf{R}) \right) \phi_k(\mathbf{R}) + \sum_{m \neq k} \theta_{km}(\mathbf{R}) \phi_m(\mathbf{R})$$

- Schrödinger's equation in the *diabatic basis*
$$i\hbar \frac{\partial}{\partial t} \phi_k(\mathbf{R}) = -\sum_n \frac{\hbar^2}{2M} \nabla_{R_n}^2 \phi_k(\mathbf{R}) + \sum_m V_{km}(|R_k - R_m|) \phi_m(\mathbf{R})$$

Schrödinger's equation



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- Hamiltonian $\hat{H}_{nuc} = -\sum_n \frac{\hbar^2 \nabla_R^2}{2M}$

$$\hat{H}_{el} = -\sum_{nm} \frac{\mu^2}{|R_n - R_m|^3} |\, s_n p_m \,\rangle \langle\, p_n s_m \,| = \sum_{n,m} V(|R_n - R_m|) |\, \pi_n \,\rangle \langle\, \pi_m \,|$$

- Schrödinger's equation in the *adiabatic basis*

$$i\hbar \frac{\partial}{\partial t} \phi_k(\mathbf{R}) = \left(\sum_n -\frac{\hbar^2}{2M} \nabla_{R_n}^2 + U_k(\mathbf{R}) \right) \phi_k(\mathbf{R}) + \sum_{m \neq k} \theta_{km}(\mathbf{R}) \phi_m(\mathbf{R})$$

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Quantum classical hybrids

- Schrödinger's equation in the *adiabatic basis*

$$i\hbar\frac{\partial}{\partial t}\phi_k(\mathbf{R}) = \underbrace{\left(\sum_n -\frac{\hbar^2}{2M}\nabla^2_{R_n} + U_k(\mathbf{R})\right)}_{\text{Motion in potential Uk}}\phi_k(\mathbf{R}) + \sum_{m\neq k}\theta_{km}(\mathbf{R})\phi_m(\mathbf{R})$$

- Assume **classical**, well defined trajectories R(t), **quantum** electronic state

$$|\,\Psi(t)\,\rangle = \sum_n \tilde{c}_n(t)|\,\varphi_n(t)\,\rangle$$

- Derive Schrödinger's equation...

$$i\hbar\frac{\partial|\,\Psi(t)\,\rangle}{\partial t} = \hat{H}(R(t))|\,\Psi(t)\,\rangle$$

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Quantum classical hybrids

- Schrödinger's equation in the *adiabatic basis*

$$i\hbar\frac{\partial}{\partial t}\phi_k(\mathbf{R}) = \underbrace{\left(\sum_n -\frac{\hbar^2}{2M}\nabla^2_{R_n} + U_k(\mathbf{R})\right)}_{\text{Motion in potential Uk}}\phi_k(\mathbf{R}) + \sum_{m\neq k}\theta_{km}(\mathbf{R})\phi_m(\mathbf{R})$$

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$$|\,\Psi(\mathbf{R},t)\,\rangle = \sum_n \phi_n(\mathbf{R},t)|\,\varphi_n(t)\,\rangle \longrightarrow |\,\Psi(t)\,\rangle = \sum_n \tilde{c}_n(t)|\,\varphi_n(t)\,\rangle$$

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Quantum classical hybrids

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$$i\hbar\frac{\partial|\,\Psi(t)\,\rangle}{\partial t} = \hat{H}(R(t))|\,\Psi(t)\,\rangle$$

$$i\hbar\frac{\partial|\,\Psi(t)\,\rangle}{\partial t} = i\hbar\sum_k \frac{\partial\tilde{c}_k(t)}{\partial t}|\,\varphi_k(t)\,\rangle + \tilde{c}_k(t)\frac{\partial|\,\varphi_k(t)\,\rangle}{\partial t} = \hat{H}(R(t))|\,\Psi(t)\,\rangle$$

Quantum classical hybrids

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- Derive Schrödinger's equation...

$$\nabla_R|\,\varphi_k(t)\,\rangle\frac{\partial R}{\partial t}$$

$$i\hbar\frac{\partial|\,\Psi(t)\,\rangle}{\partial t} = \hat{H}(R(t))|\,\Psi(t)\,\rangle$$

$$i\hbar\frac{\partial|\,\Psi(t)\,\rangle}{\partial t} = i\hbar\sum_k \frac{\partial\tilde{c}_k(t)}{\partial t}|\,\varphi_k(t)\,\rangle + \tilde{c}_k(t)\frac{\partial|\,\varphi_k(t)\,\rangle}{\partial t} = \hat{H}(R(t))|\,\Psi(t)\,\rangle$$

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- Derive Schrödinger's equation...

$$\nabla_R|\,\varphi_k(t)\,\rangle\frac{\partial R}{\partial t}$$ atomic velocity

$$i\hbar\frac{\partial|\,\Psi(t)\,\rangle}{\partial t} = \hat{H}(R(t))|\,\Psi(t)\,\rangle$$

$$i\hbar\frac{\partial|\,\Psi(t)\,\rangle}{\partial t} = i\hbar\sum_k\frac{\partial\tilde{c}_k(t)}{\partial t}|\,\varphi_k(t)\,\rangle + \tilde{c}_k(t)\frac{\partial|\,\varphi_k(t)\,\rangle}{\partial t} = \hat{H}(R(t))|\,\Psi(t)\,\rangle$$

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Quantum classical hybrids

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- Derive Schrödinger's equation...

$$i\hbar\frac{\partial|\,\Psi(t)\,\rangle}{\partial t} = \hat{H}(R(t))|\,\Psi(t)\,\rangle$$

$$\nabla_R|\,\varphi_k(t)\,\rangle\frac{\partial R}{\partial t} \quad \text{atomic velocity}$$

$$i\hbar\frac{\partial|\,\Psi(t)\,\rangle}{\partial t} = i\hbar\sum_k\frac{\partial\tilde{c}_k(t)}{\partial t}|\,\varphi_k(t)\,\rangle + \tilde{c}_k(t)\frac{\partial|\,\varphi_k(t)\,\rangle}{\partial t} = \hat{H}(R(t))|\,\Psi(t)\,\rangle$$

- ...for the coefficient of exciton k

$$i\hbar\dot{\tilde{c}}_k(t) = U_k(R(t))\tilde{c}_k(t) + i\hbar\sum_m\langle\,\varphi_k(t)\,|\,\nabla_R\varphi_m(t)\,\rangle\tilde{c}_m(t)\frac{\partial R}{\partial t}$$

Tully's surface hopping

- Schrödinger's equation in the *adiabatic basis*

$$i\hbar\frac{\partial}{\partial t}\phi_k(\mathbf{R}) = \left(\sum_n -\frac{\hbar^2}{2M}\nabla^2_{R_n} + U_k(\mathbf{R})\right)\phi_k(\mathbf{R}) + \sum_{m\neq k}\theta_{km}(\mathbf{R})\phi_m(\mathbf{R})$$

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- Classical motion in potential Uk

$$M\ddot{\mathbf{R}}(t) = -\nabla_R U_k(\mathbf{R})$$

k stochastic!
multiple trajectories

mpipks Finite Systems

Tully's surface hopping

- Schrödinger's equation in the *adiabatic basis*

$$i\hbar\frac{\partial}{\partial t}\phi_k(\mathbf{R}) = \left(\sum_n -\frac{\hbar^2}{2M}\nabla^2_{R_n} + U_k(\mathbf{R})\right)\phi_k(\mathbf{R}) + \sum_{m\neq k}\theta_{km}(\mathbf{R})\phi_m(\mathbf{R})$$

- Classical motion in potential Uk

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- Populate in general *multiple* excitons, propagate motion only on *single* surface.
  For consistency: *J.C. Tully and R. K. Preston, J. Chem. Phys.,* ***55*** *562 (1971).*

jump $k \rightarrow m$ with probability $\max\left(0, \frac{-2\mathrm{Re}[\tilde{c}_k^*\tilde{c}_m\dot{\mathbf{R}}\cdot\mathbf{d}_{km}]\Delta t}{|\tilde{c}_k(t)|^2}\right)$

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Finite Systems

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- Tully's fewest switching algorithm: Ensures $\overline{|\tilde{c}_n(t)|^2} = \overline{[\#\text{trajectories on surface n}](t)}$

Example

- Three coupled electronic states

$$\hat{H}_{el} = \begin{pmatrix} 0 & \chi(x) & 0 \\ \chi(x) & E_0 - \epsilon(x) & \chi(x) \\ 0 & \chi(x) & 2(E_0 - \epsilon(x)) \end{pmatrix}$$

- Wavepacket initially on lowest surface

- Quantum solution (shown), Tully compares very well (not shown)

*J.C. Tully and R. K. Preston, J. Chem. Phys., **55** 562 (1971).*

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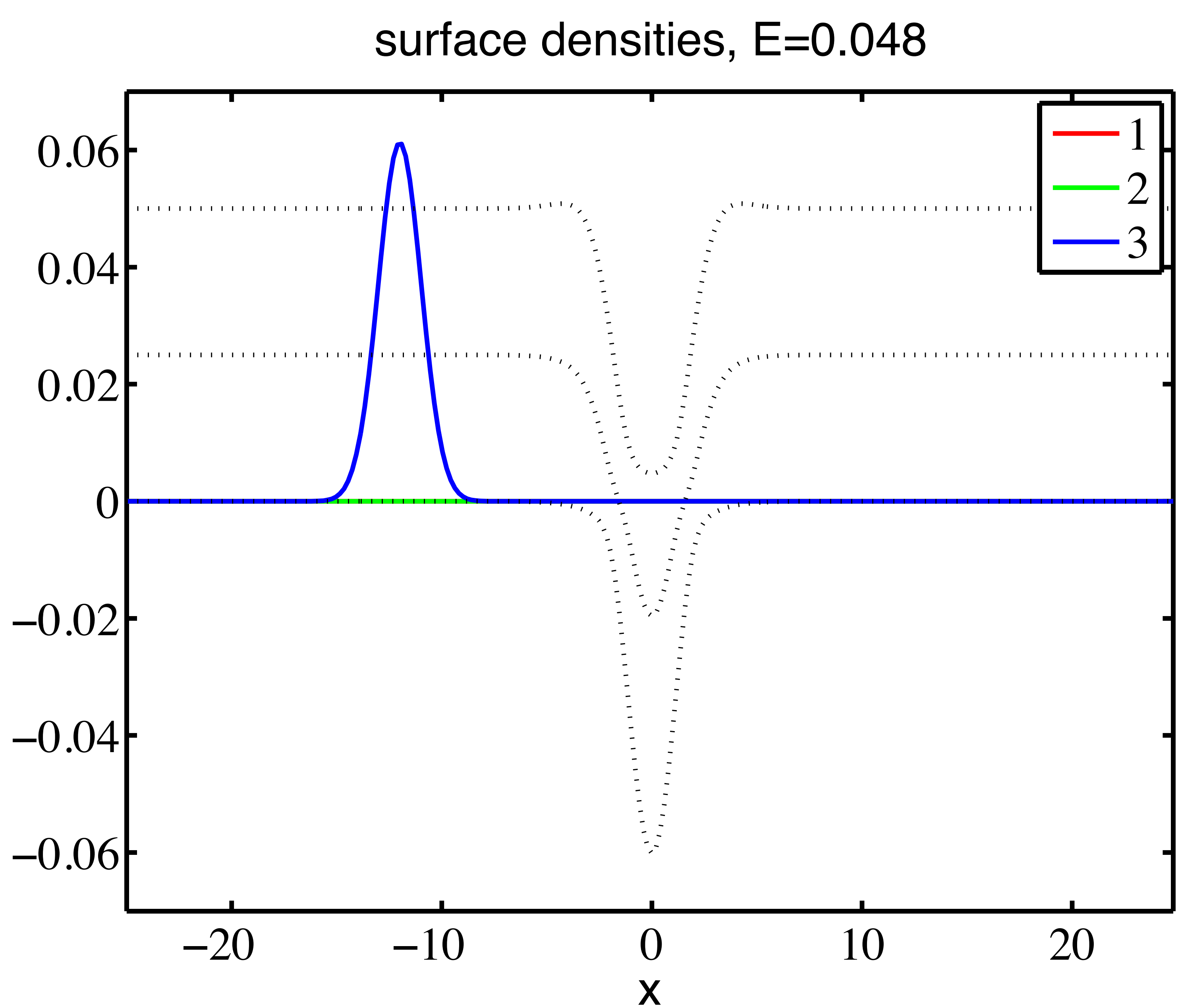

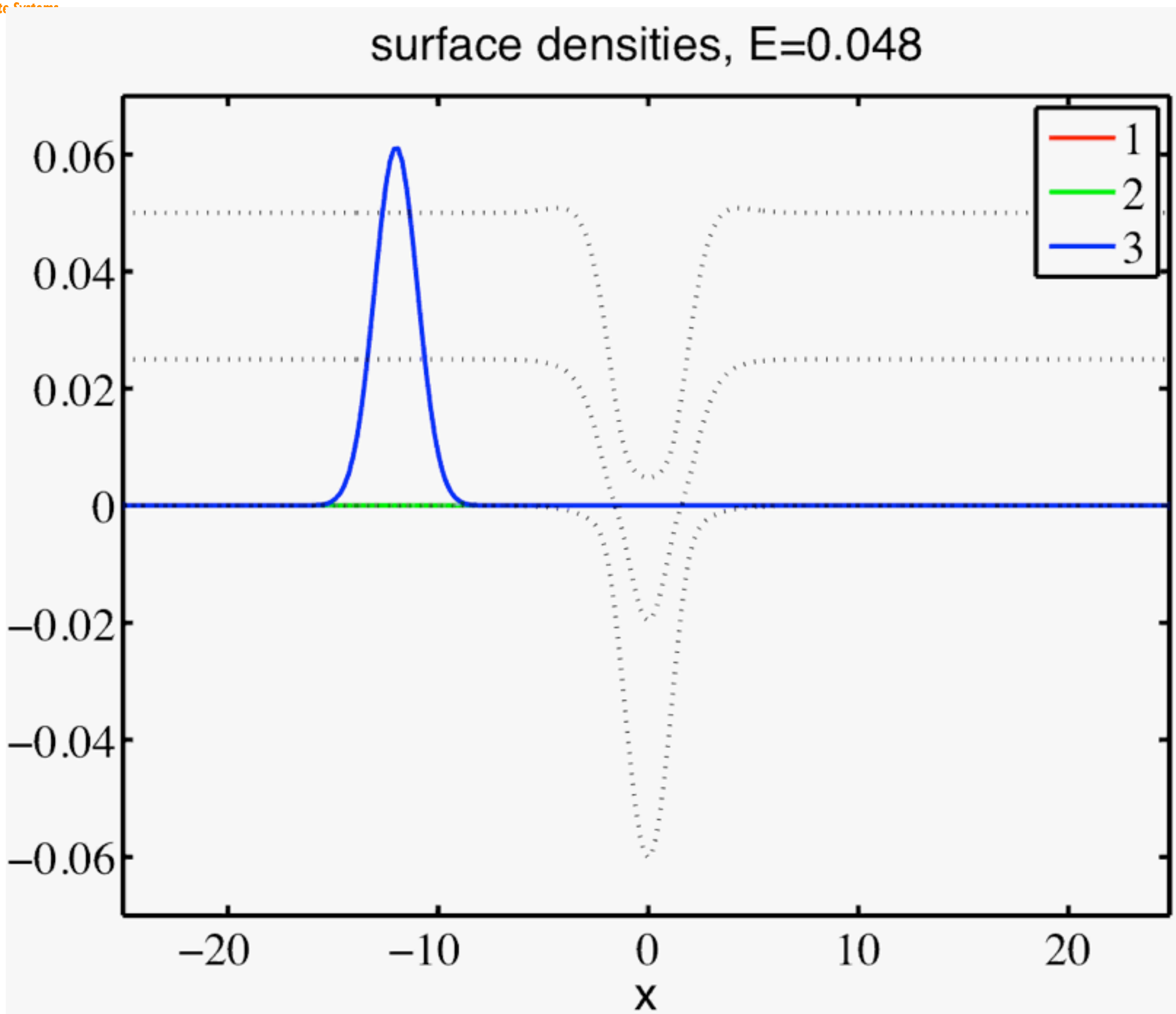
surface densities, E=0.048
0.06
0.04
0.02
0
−0.02
−0.04
−0.06
−20
−10
0
10
20
x
1
2
3

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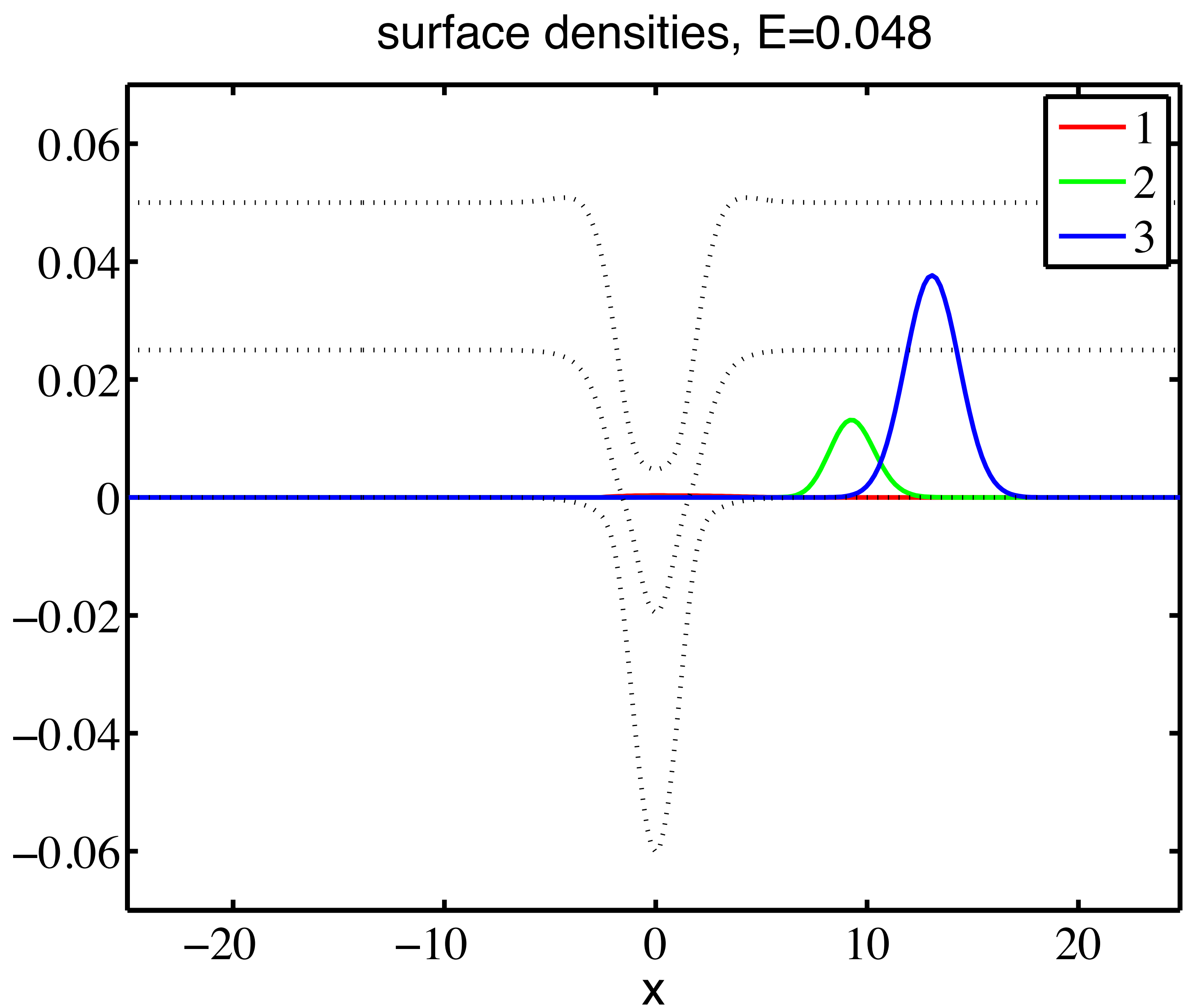
- Adjust velocity when jumping, to conserve energy

*S. Hammes-Schiffer and J.C. Tully , J. Chem. Phys., **101** 4657 (1994).*



Ehrenfest method

- Single particle quantum mechanics, Ehrenfest theorem:

$$\langle \dot{\hat{p}} \rangle = -\langle \nabla V(\hat{R}) \rangle$$

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(Tully) $$M\ddot{\mathbf{R}}(t) = -\nabla_R U_k(\mathbf{R})$$

(Ehrenfest) $$M\ddot{\mathbf{R}}(t) = -\langle \Psi | \nabla_R \hat{H}_{el}(\mathbf{R}) | \Psi \rangle$$

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- Does not allow for correlations between BO surface and quantum state, see *example...*

Example

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$$\hat{H}_{el} = \begin{pmatrix} 0 & \chi(x) & 0 \\ \chi(x) & E_0 - \epsilon(x) & \chi(x) \\ 0 & \chi(x) & 2(E_0 - \epsilon(x)) \end{pmatrix}$$

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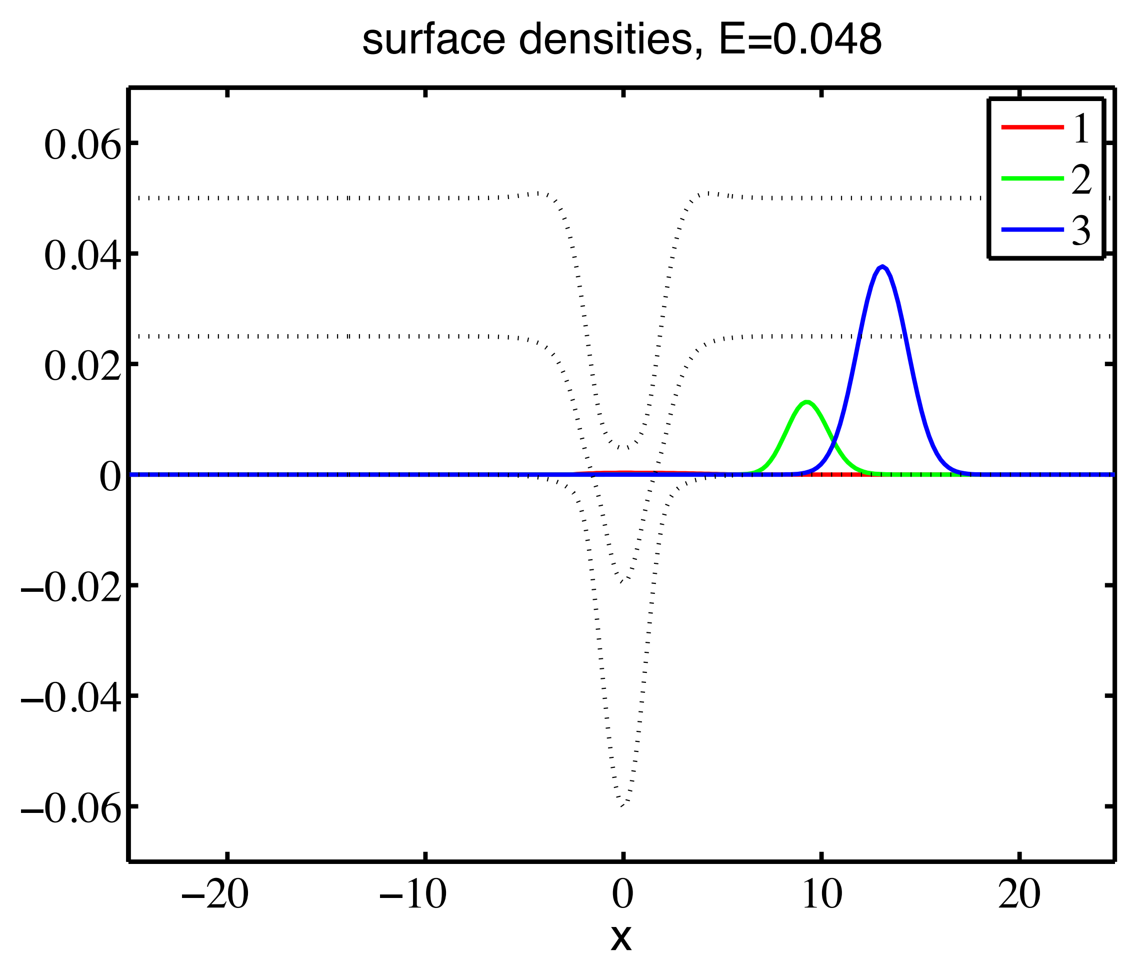

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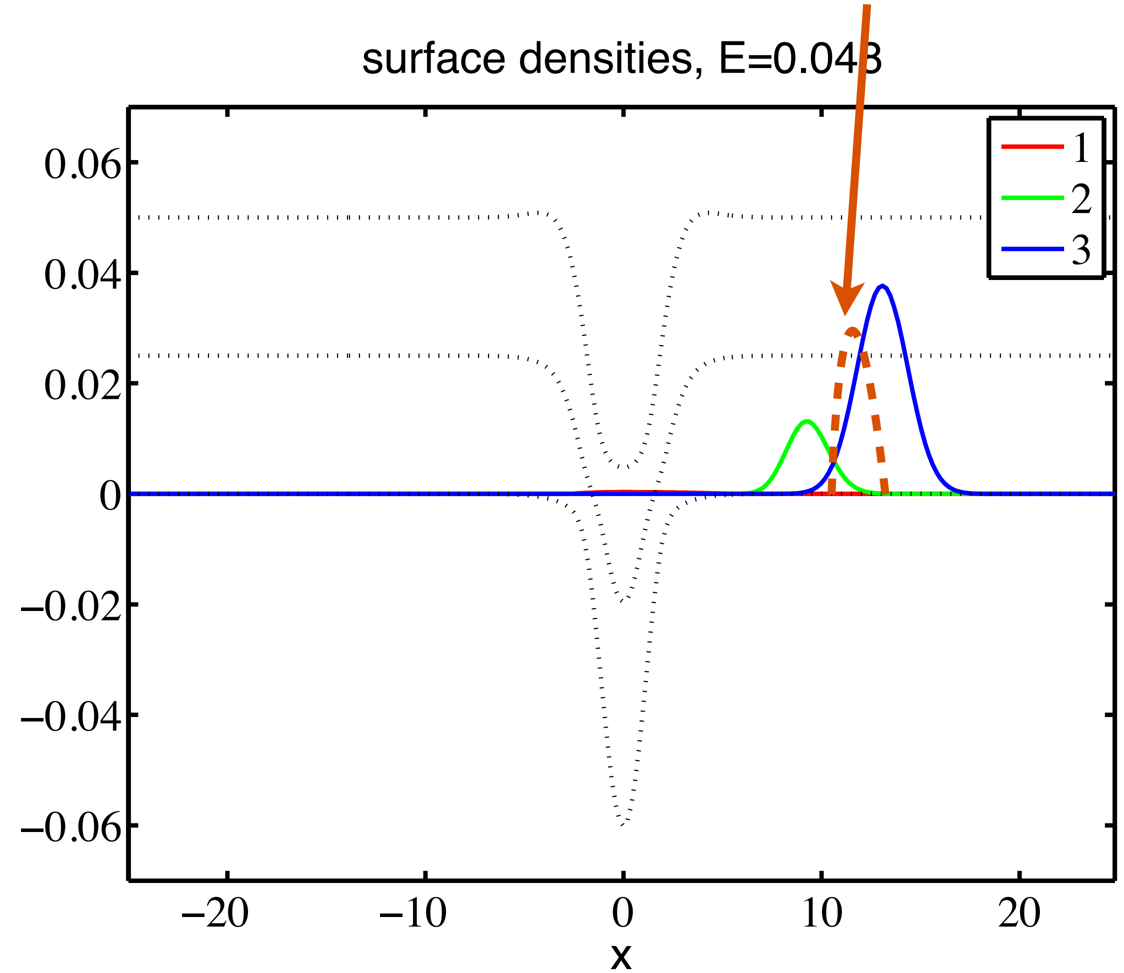
Ehrenfest result



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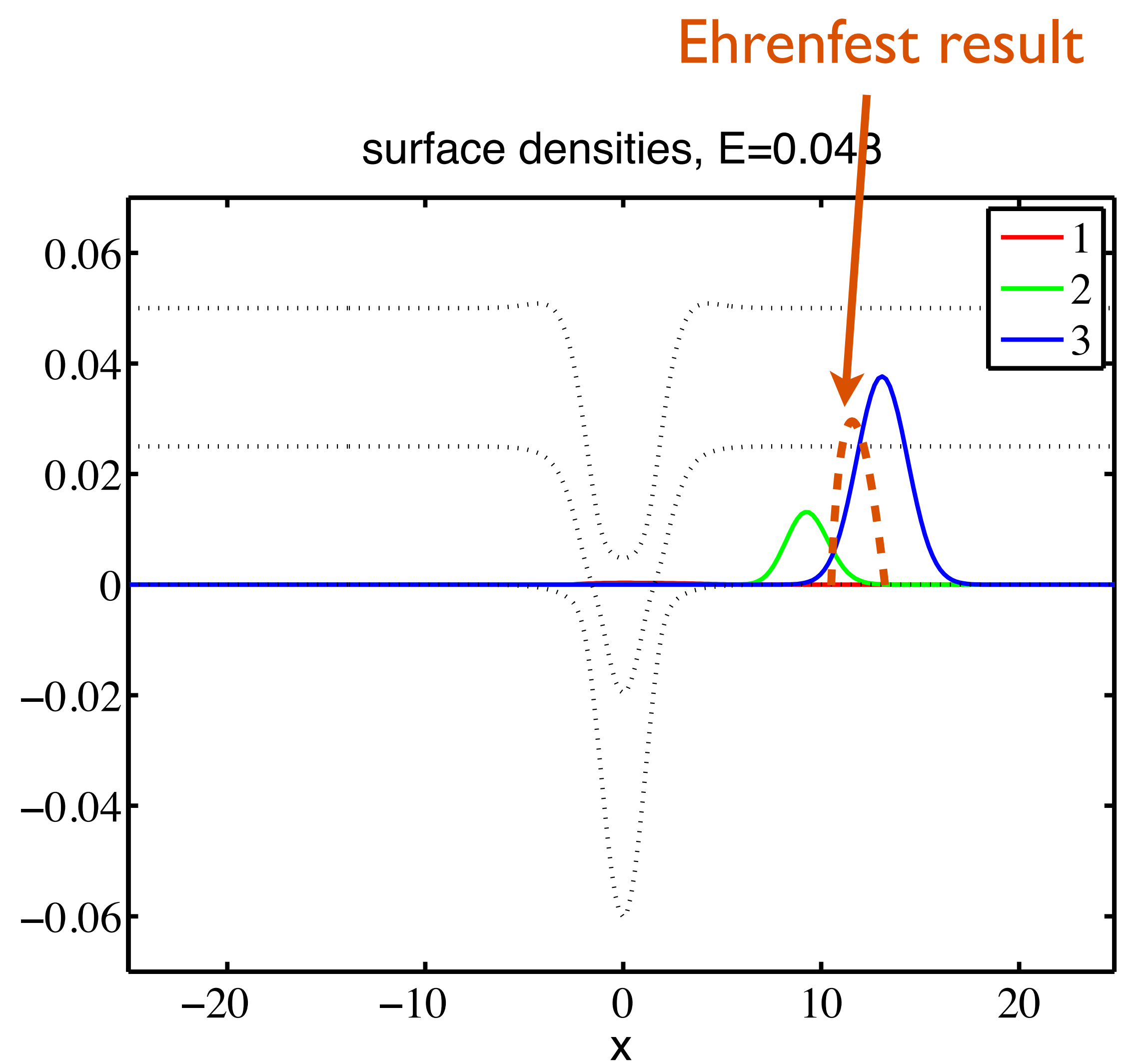
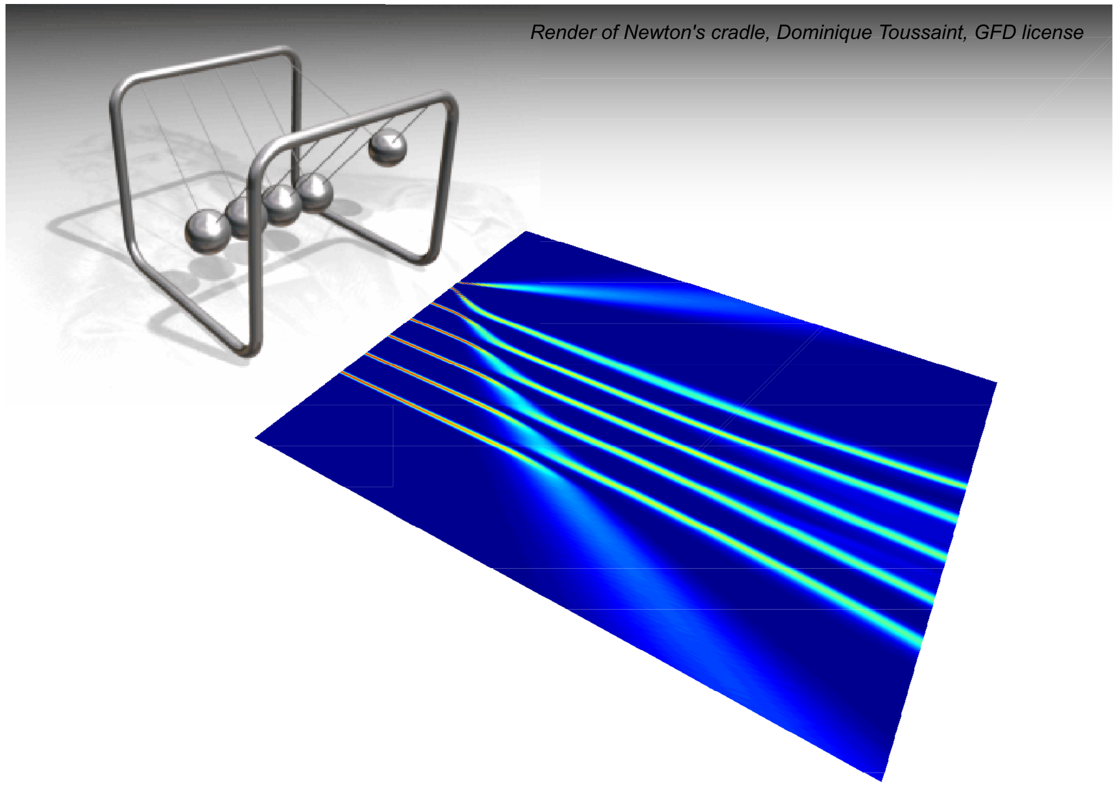
- Different final velocities on surfaces 3 and 2

- Ehrenfest method cannot capture these essential features



(4) Entanglement

(4a) transport



Entanglement: more than correlation

Entangled state cannot be factorized

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left(|sp\rangle + |ps\rangle \right) \neq |\phi_1\rangle \otimes |\phi_2\rangle$$

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EPR (**E**instein **P**odolski **R**osen) Scenario (Bohm variant)

A. Einstein et al. *Phys. Rev.* ***47*** *777 (1935).*

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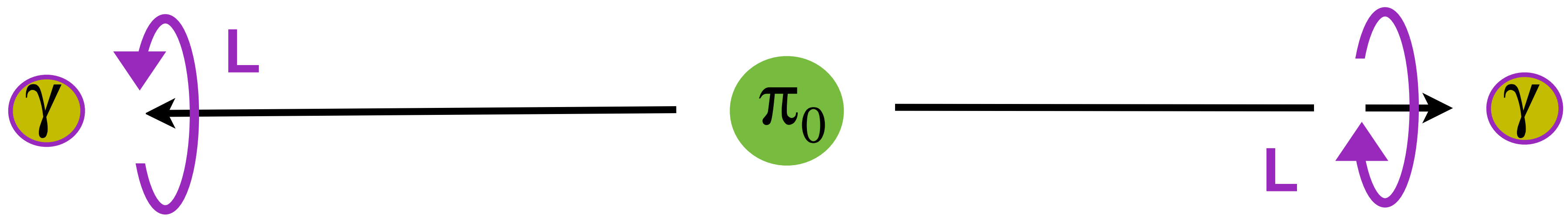

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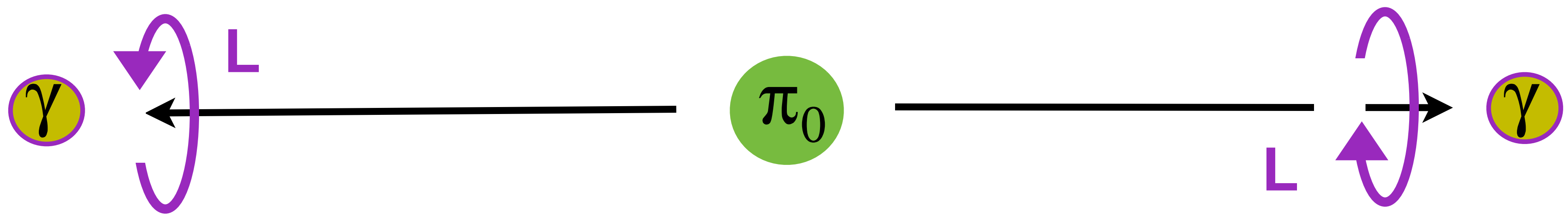

Bell-state $|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|LL\rangle - |RR\rangle\right)$

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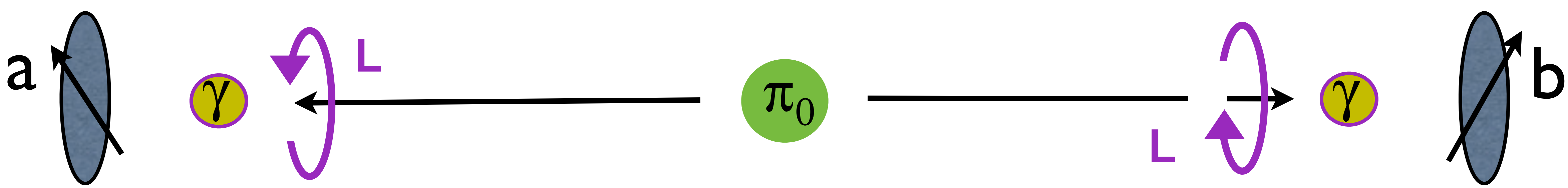

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Bell-inequalities $\quad |C^{(\mathbf{a},\mathbf{b})} + C^{(\mathbf{a},\mathbf{b}')} + C^{(\mathbf{a}',\mathbf{b})} - C^{(\mathbf{a}',\mathbf{b}')}| \leq 2$

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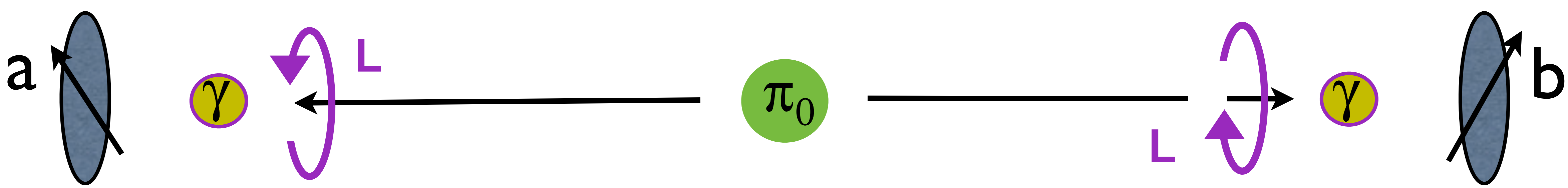

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J.F.Clauser et al. *Phys. Rev. Lett.* ***23*** *880 (1969).*

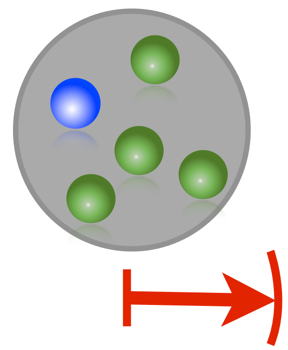
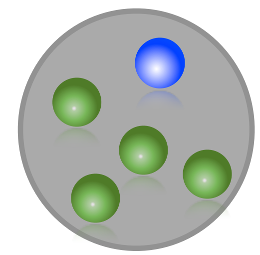
Entanglement **more** than correlations (Bell's theorem)

J.S.Bell Physics ***1*** *195 (1964).*

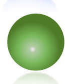
QM: $|\sum C| = 2\sqrt{2}$

Entanglement in Rydberg physics

Blockade state

$|\Psi_{block}\rangle = \frac{1}{\sqrt{N}}\Big(|$  $\rangle + |$  $\rangle + \cdots\Big)$

$|s$  $\rangle$

$|g$  $\rangle$

r_b Blockade radius

Entanglement in Rydberg physics

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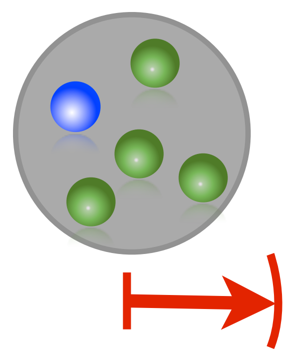
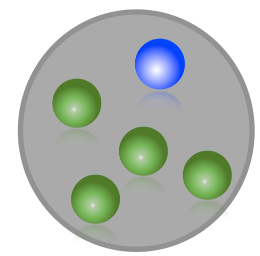
$$|\,\Psi_{block}\,\rangle = \frac{1}{\sqrt{N}}\left(|\right.$$  $$\left.\rangle + |\right.$$  $$\left.\rangle + \cdots\right)$$

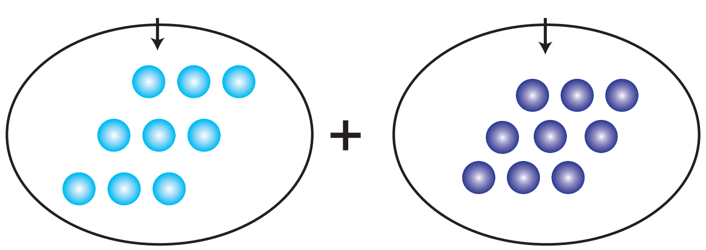
$|\,s\,\rangle$

$|\,g\,\rangle$

GHZ state

Blockade as tool

requires two Rydberg states with quite different interactions



M. Saffman and K. Mølmer, Phys. Rev. Lett. ***102****, 240502 (2009).*

Entanglement in Rydberg physics

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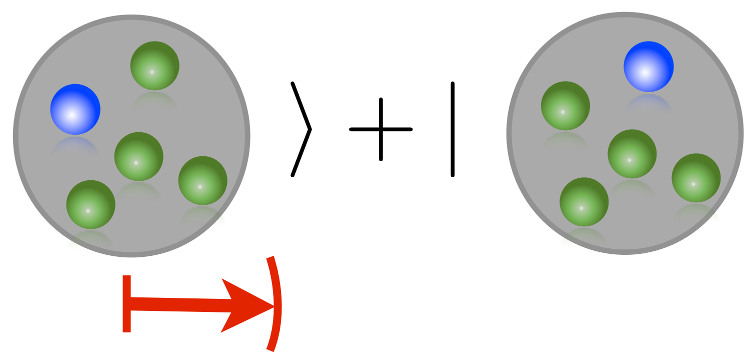

$|s\rangle$

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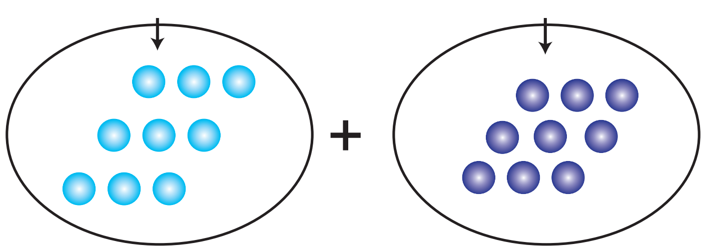

M. Saffman and K. Mølmer, Phys. Rev. Lett. ***102****, 240502 (2009).*

Mesoscopic Q-gate

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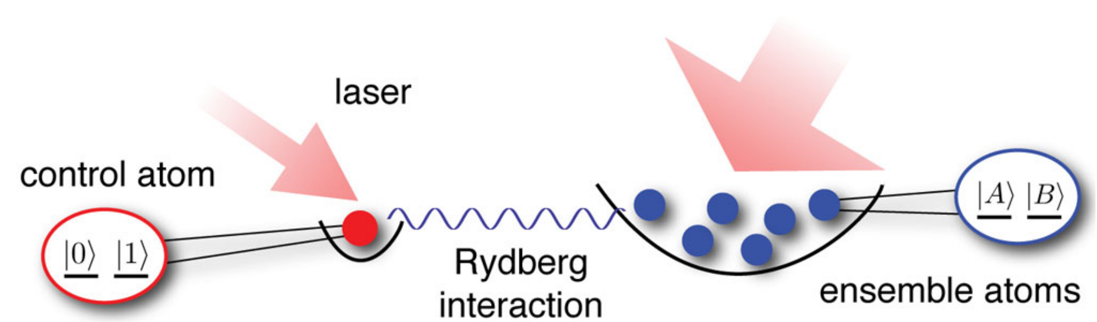


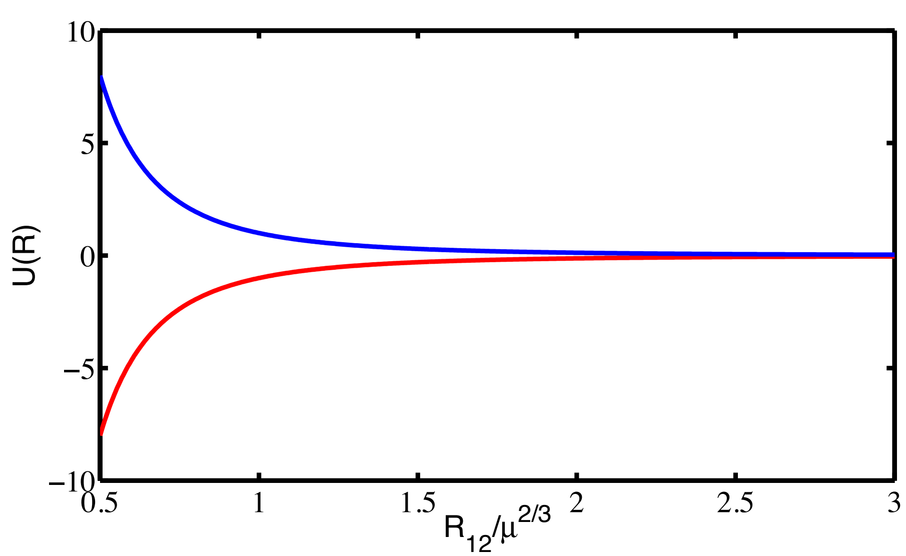
M. Müller, I. Lesanovsky, H. Weimer, H. P. Büchler, and P. Zoller, Phys. Rev. Lett. ***102****, 170502 (2009).*

Dimer excitons = Bell states

Bell-states: Maximally entangled two qubit states

$$\{|\,Bell\,\rangle\} = \{\frac{1}{\sqrt{2}}\,(|\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle)\,,\,\frac{1}{\sqrt{2}}\,(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle)\,,$$
$$\frac{1}{\sqrt{2}}\,(|\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle)\,,\,\frac{1}{\sqrt{2}}\,(|\uparrow\downarrow\rangle + |\uparrow\downarrow\rangle)\}$$

Dimer Excitons:



"attractive" eigenstate (exciton)

$$|\varphi_1\rangle = \frac{1}{\sqrt{2}}\,(|sp\rangle + |ps\rangle)$$

"repulsive" eigenstate (exciton)

$$|\varphi_2\rangle = \frac{1}{\sqrt{2}}\,(|sp\rangle - |ps\rangle)$$

Rydberg angular momentum = pseudo-spin $\quad |\,s\,\rangle \rightarrow |\downarrow\rangle \qquad |\,p\,\rangle \rightarrow |\uparrow\rangle$

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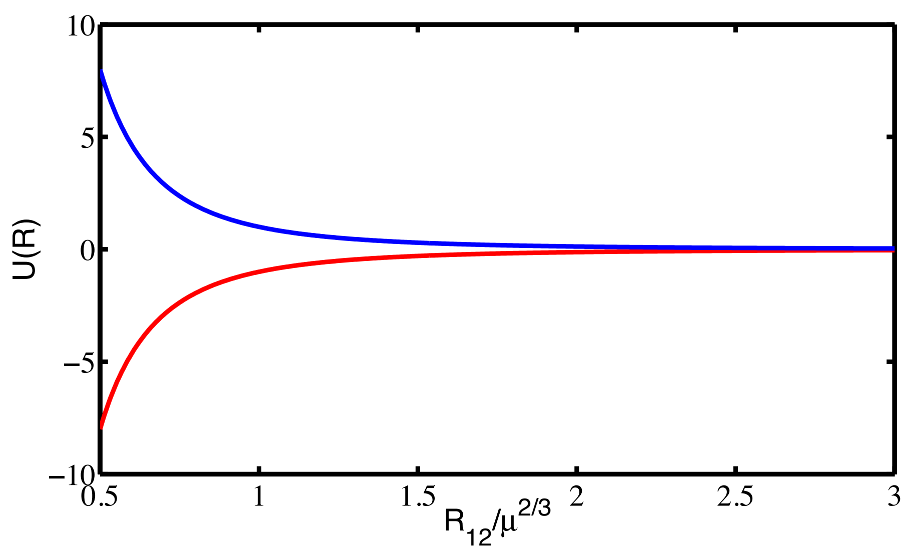
Dimer Excitons:



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depends on sign of V, choose via states

Rydberg angular momentum = pseudo-spin $|\,s\,\rangle \rightarrow |\downarrow\rangle$ $|\,p\,\rangle \rightarrow |\uparrow\rangle$

Entanglement tuning through exciton localisation

$$H^{\mathrm{el}}(\mathbf{R})|\,\varphi_n(\mathbf{R})\,\rangle = U_n(\mathbf{R})|\,\varphi_n(\mathbf{R})\,\rangle \qquad |\,\varphi_n(\mathbf{R})\,\rangle = \sum_m c_{n,m}|\pi_m\rangle$$

Entanglement tuning through exciton localisation

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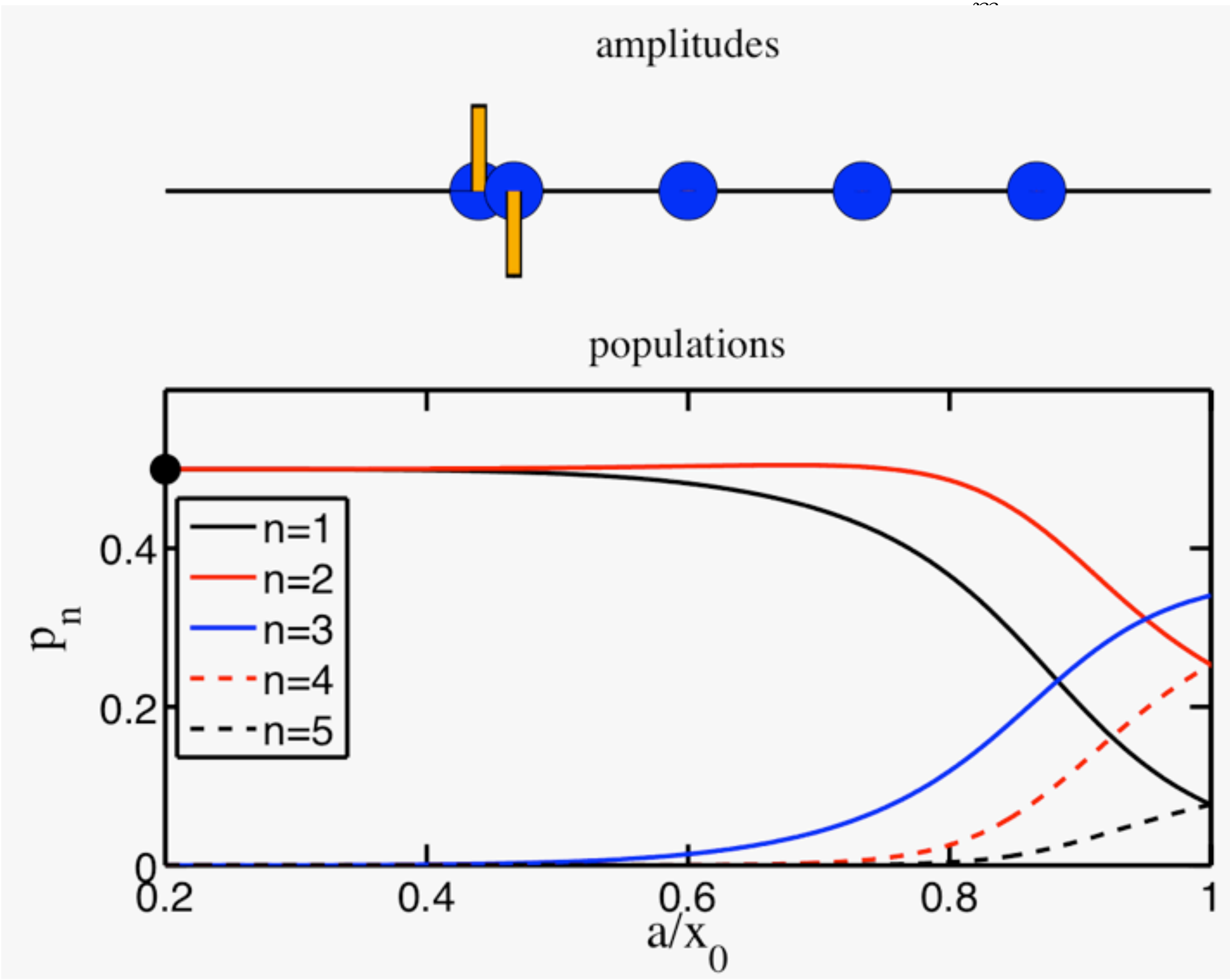
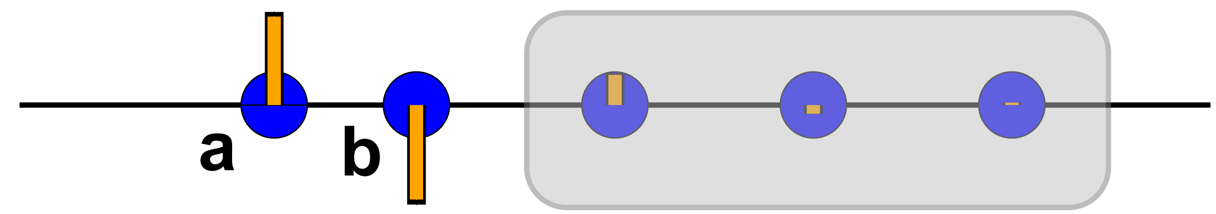


Entanglement in subsystems

Trace over all but **a** and **b**



Reduced binary density matrix

$$\hat{\beta}_{ab} = \mathrm{Tr}^{\{a,b\}}\left[\hat{\sigma}\right]$$

$$\begin{array}{cccc} |\,pp\,\rangle & |\,ps\,\rangle & |\,sp\,\rangle & |\,ss\,\rangle \end{array}$$

$$\hat{\beta} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \sigma_{aa} & \sigma_{ba} & 0 \\ 0 & \sigma_{ab} & \sigma_{bb} & 0 \\ 0 & 0 & 0 & \sum_{c\neq\{a,b\}} \sigma_{cc} \end{pmatrix}$$

Concurrence/ coherence $\quad C_{ab} = 2|\sigma_{ab}|$

Entanglement (of formation) $\quad 0 \leq E_{ab}(C_{ab}) \leq 1$

*S. Hill and W. K. Wooters, Phys. Rev. Lett. , **78** 5022 (1997).*

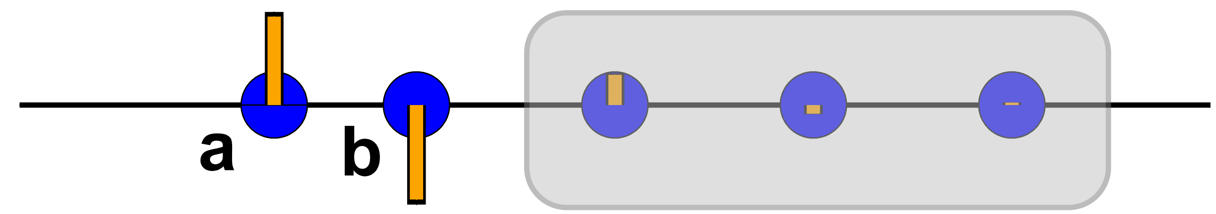
Examples:

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle + |ps\rangle\right) \qquad E = 1$$

$$|\Psi\rangle = \frac{1}{2}\left(|sp\rangle + |ps\rangle\right) + \frac{1}{\sqrt{2}}|ss\rangle \qquad E = 0.35$$

Entanglement in subsystems

Trace over all but **a** and **b**



Reduced binary density matrix

$$\hat{\beta}_{ab} = \mathrm{Tr}^{\{a,b\}}\left[\hat{\sigma}\right]$$

$$\hat{\beta} = \begin{array}{c} \begin{array}{cccc} |\,pp\,\rangle & |\,ps\,\rangle & |\,sp\,\rangle & |\,ss\,\rangle \end{array} \\ \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \sigma_{aa} & \sigma_{ba} & 0 \\ 0 & \sigma_{ab} & \sigma_{bb} & 0 \\ 0 & 0 & 0 & \sum_{c \neq \{a,b\}} \sigma_{cc} \end{pmatrix} \end{array}$$

Concurrence/ coherence $\quad C_{ab} = 2|\sigma_{ab}|$

Entanglement (of formation) $\quad 0 \leq E_{ab}(C_{ab}) \leq 1$

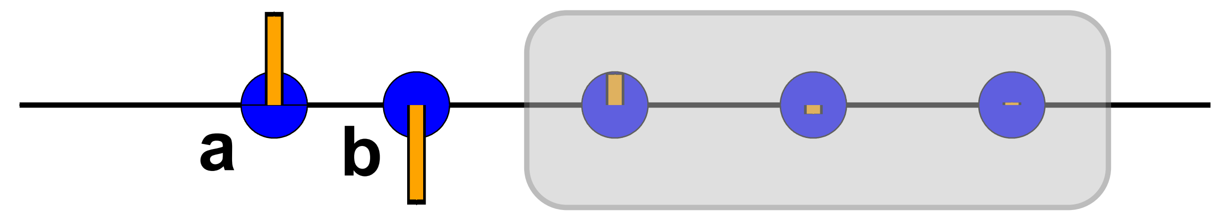
S. Hill and W. K. Wooters, Phys. Rev. Lett., ***78*** *5022 (1997).*

Examples: $\quad |\Psi\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle + |ps\rangle\right) \qquad E = 1$

$$|\Psi\rangle = \frac{1}{2}\left(|sp\rangle + |ps\rangle\right) + \frac{1}{\sqrt{2}}|ss\rangle \qquad E = 0.35$$

Entanglement in subsystems

Trace over all but **a** and **b**



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Entanglement in subsystems

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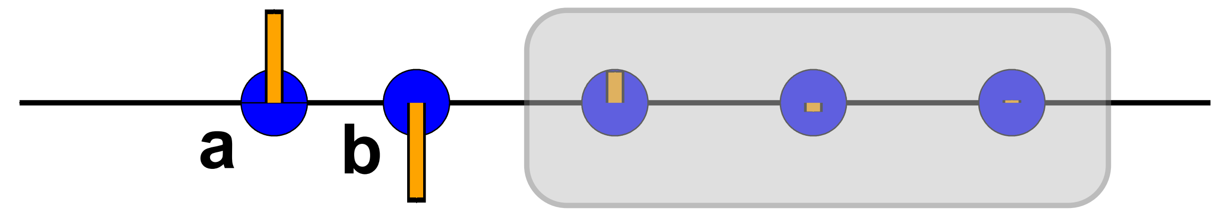

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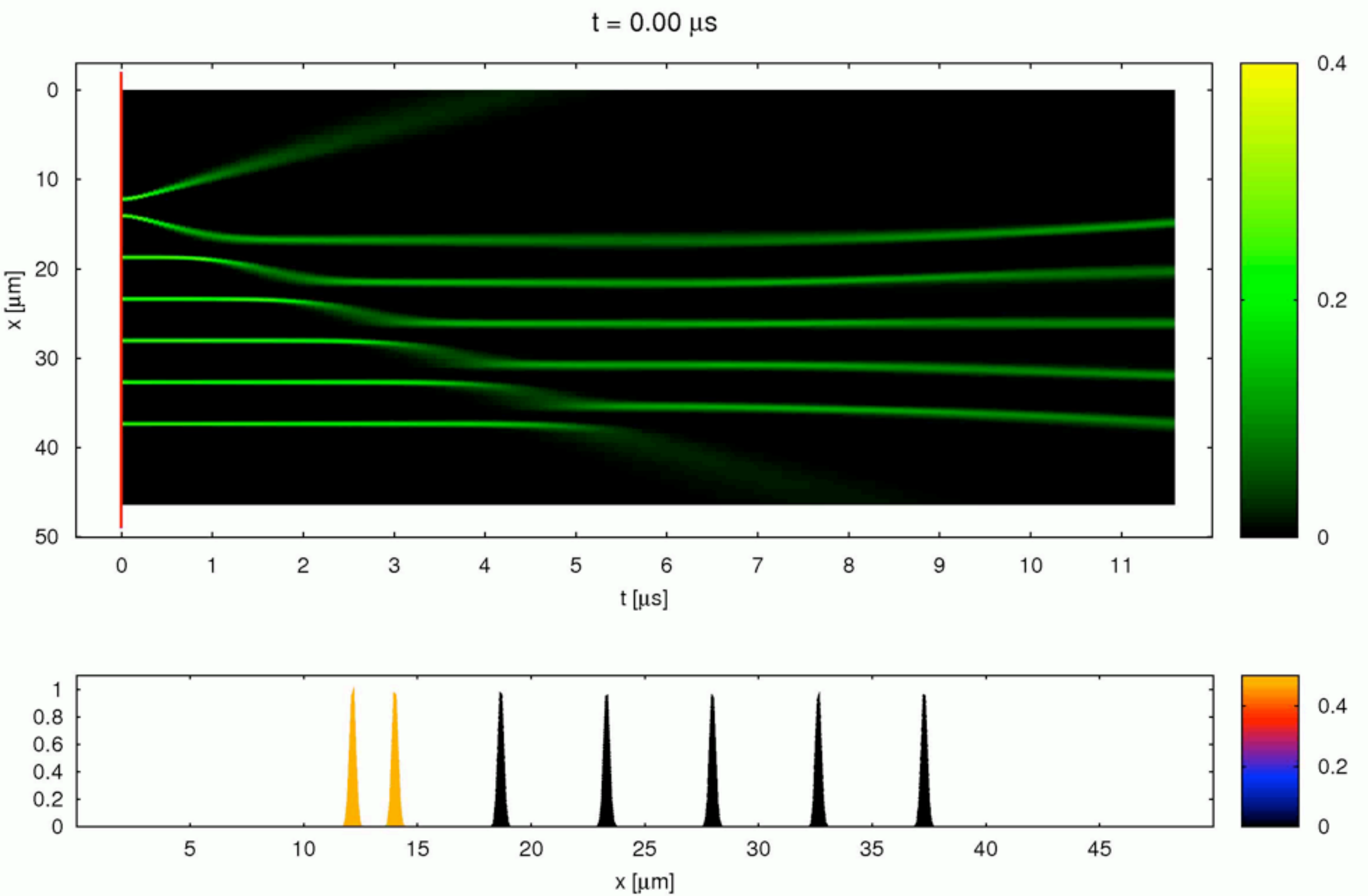
Exciton propagation through chain

Exciton propagation through chain



Exciton propagation through chain

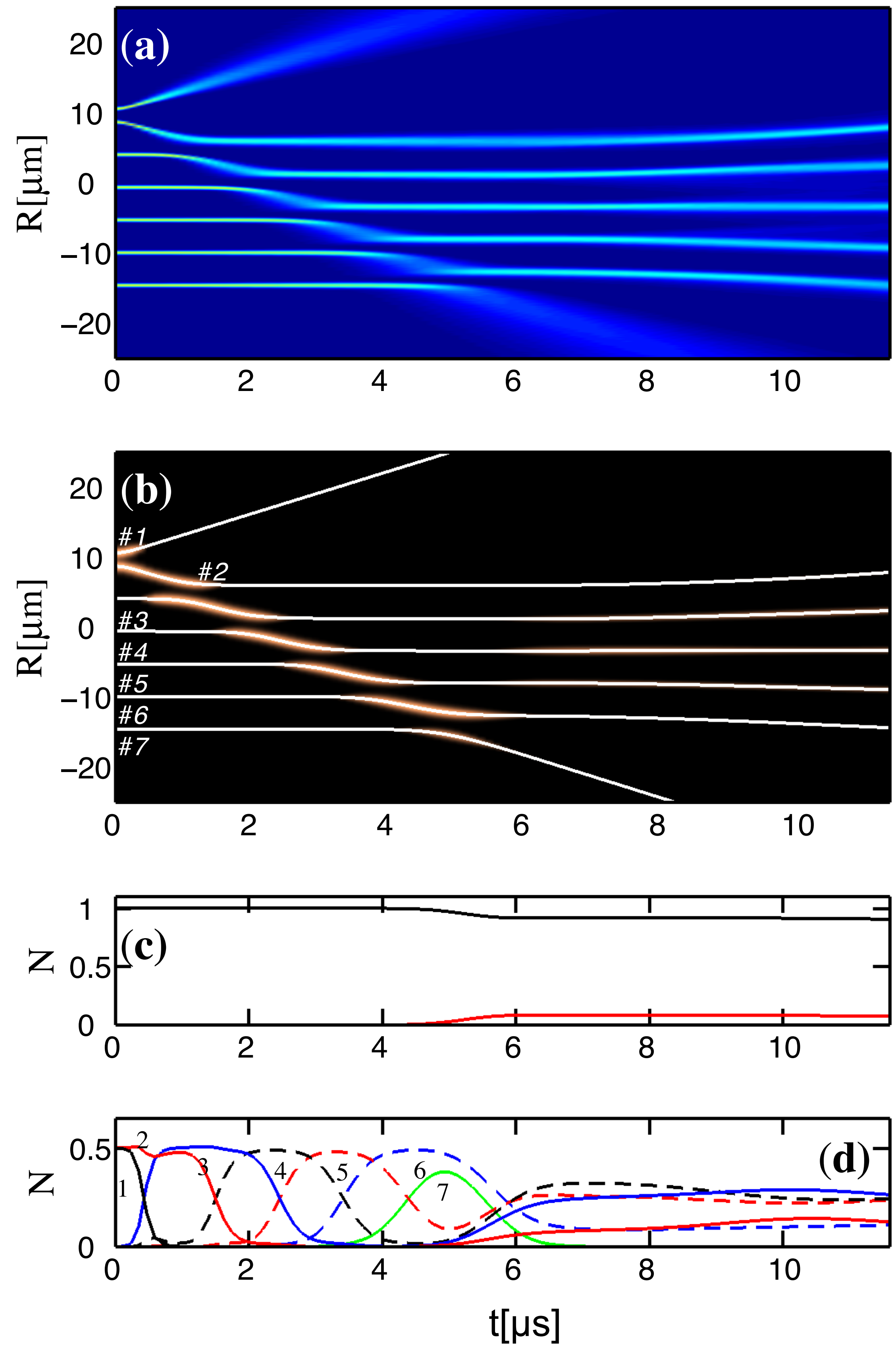
*S. Wüster, C. Ates, A. Eisfeld, J.-M. Rost, Phys. Rev. Lett. **105** 053004 (2010).*

Total density

Mean positions
&
Mean excitation

population on
adiabatic surfaces

population on
individual atoms



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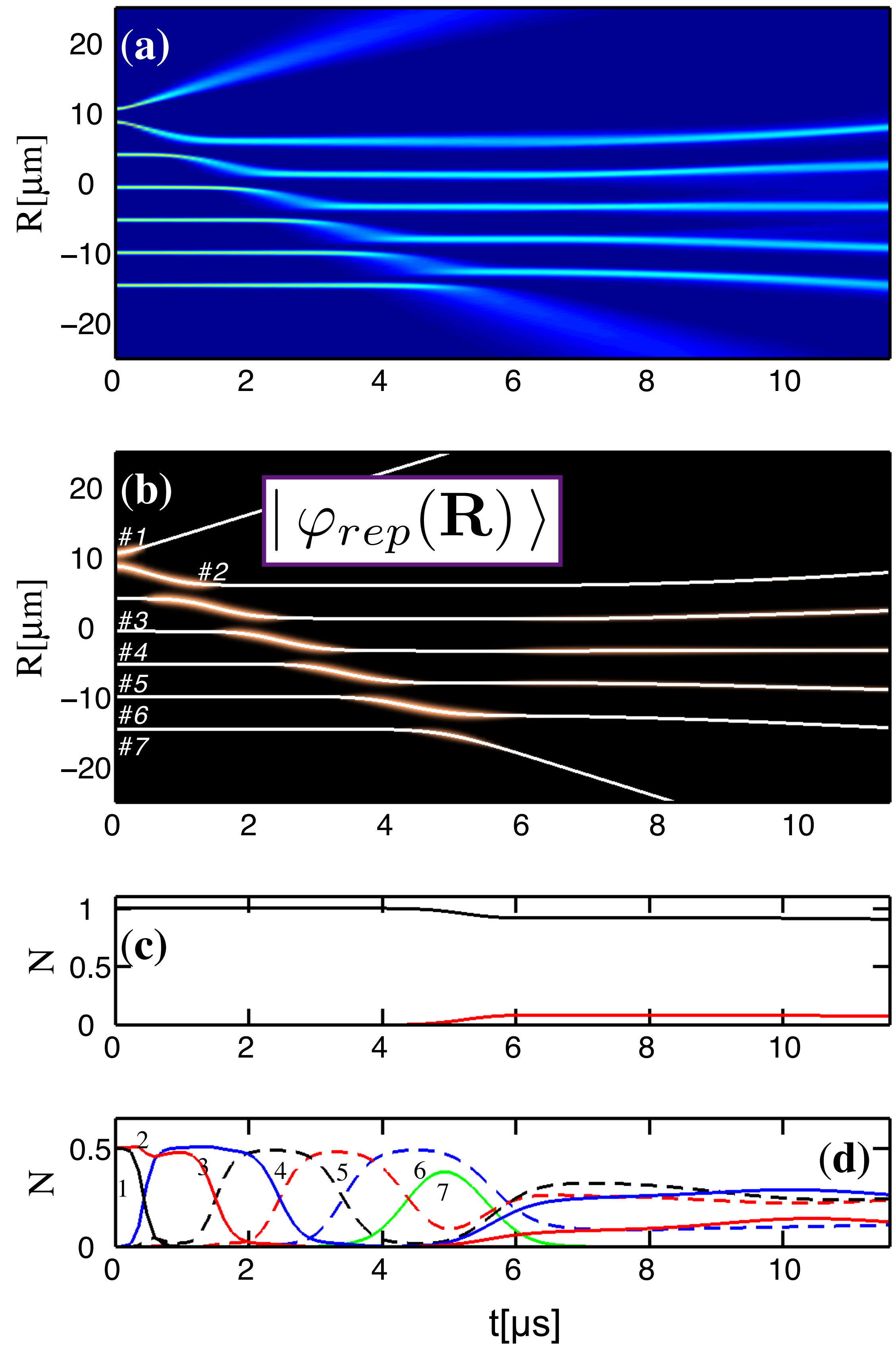

Exciton propagation through chain

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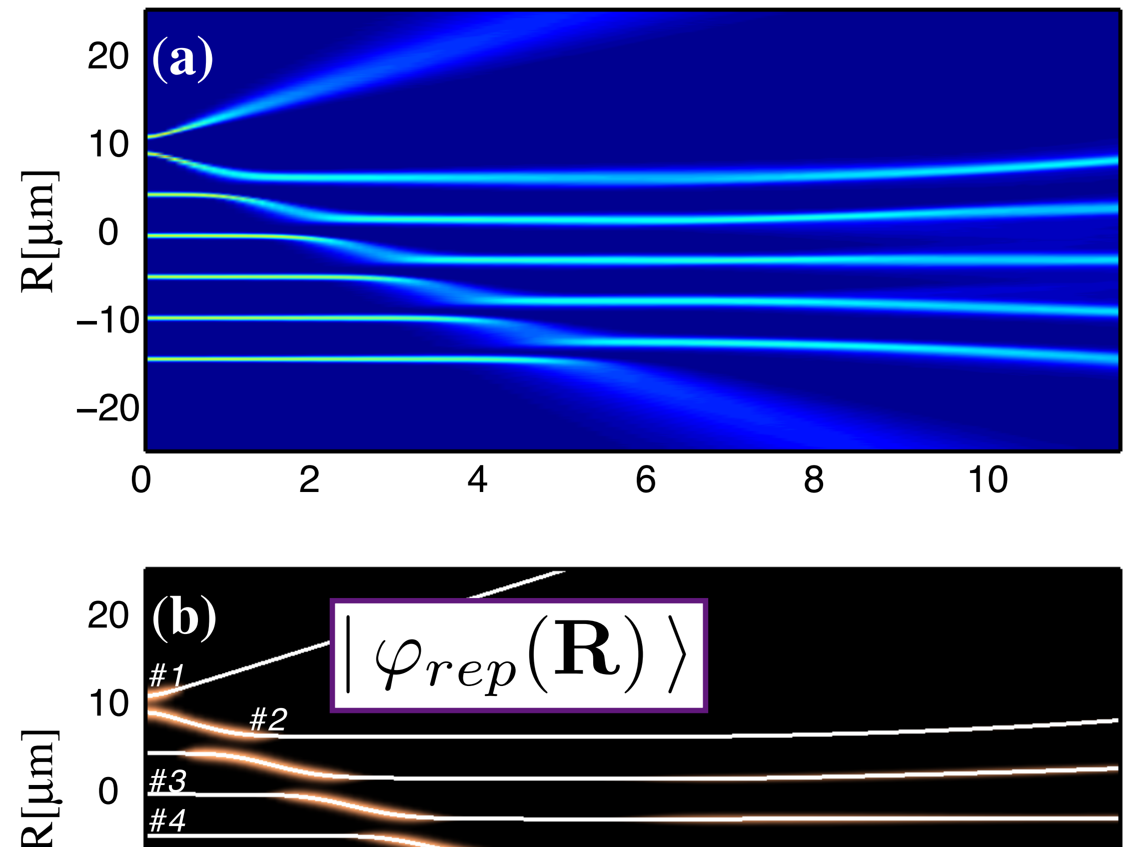
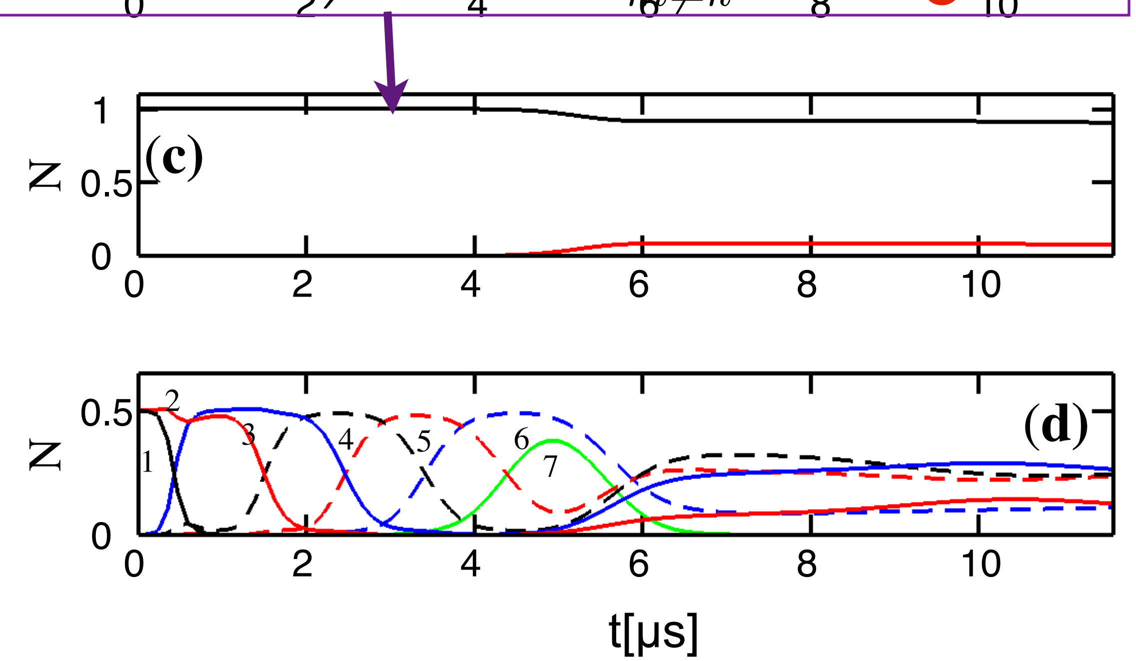


$$i\hbar\frac{\partial}{\partial t}\phi_k(\mathbf{R}) = \left(\sum_n -\frac{\hbar^2}{2M}\nabla^2_{R_n} + U_k(\mathbf{R})\right)\phi_k(\mathbf{R}) + \sum_{m\neq k}\theta_{km}(\mathbf{R})\phi_m(\mathbf{R})$$

≈ 0

population on
adiabatic surfaces

population on
individual atoms



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S. Wüster, C. Ates, A. Eisfeld, J.-M. Rost,
Phys. Rev. Lett. ***105*** *053004 (2010).*

Total density

Mean positions
&

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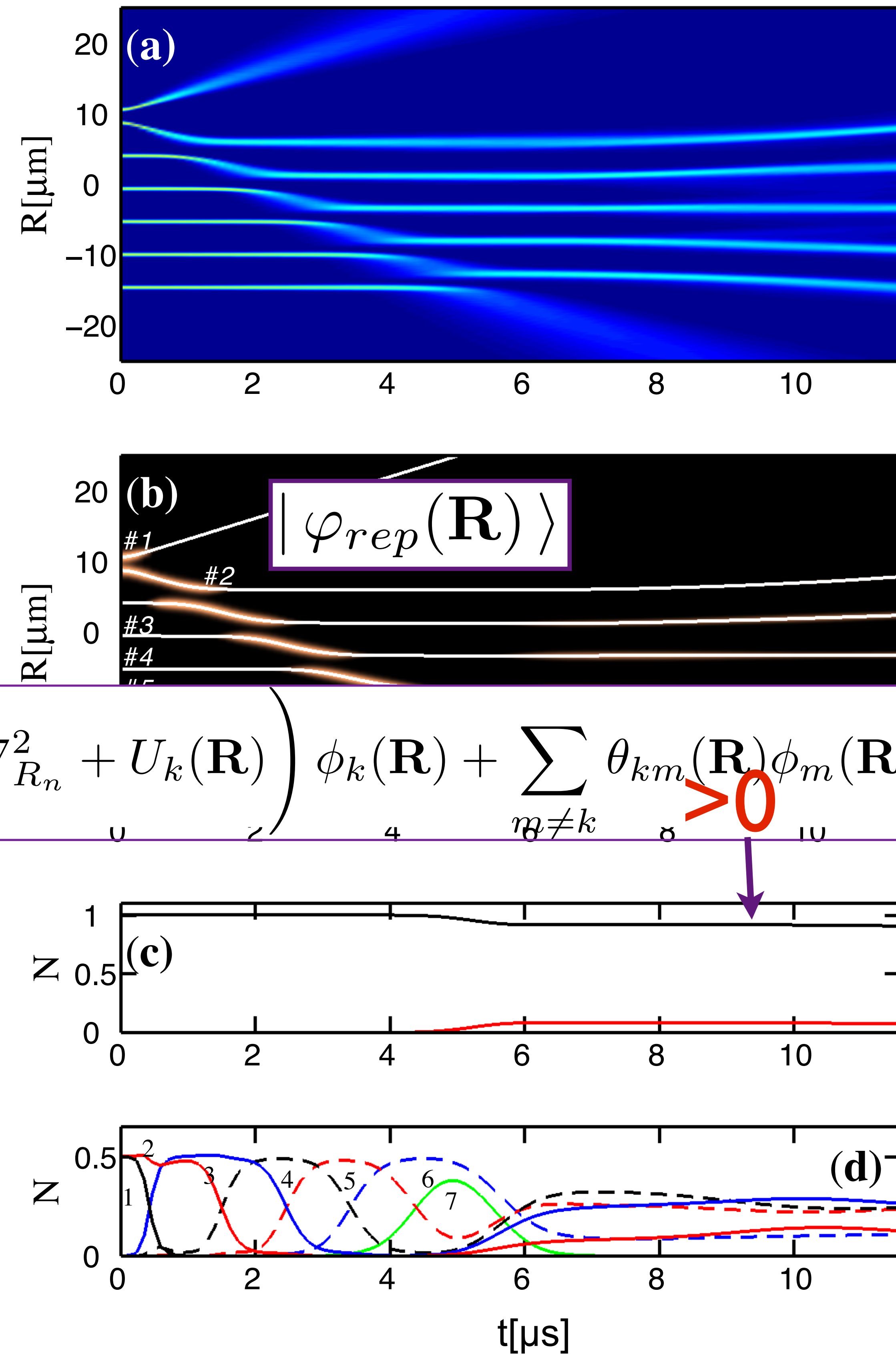
>0

population on
adiabatic surfaces

population on
individual atoms

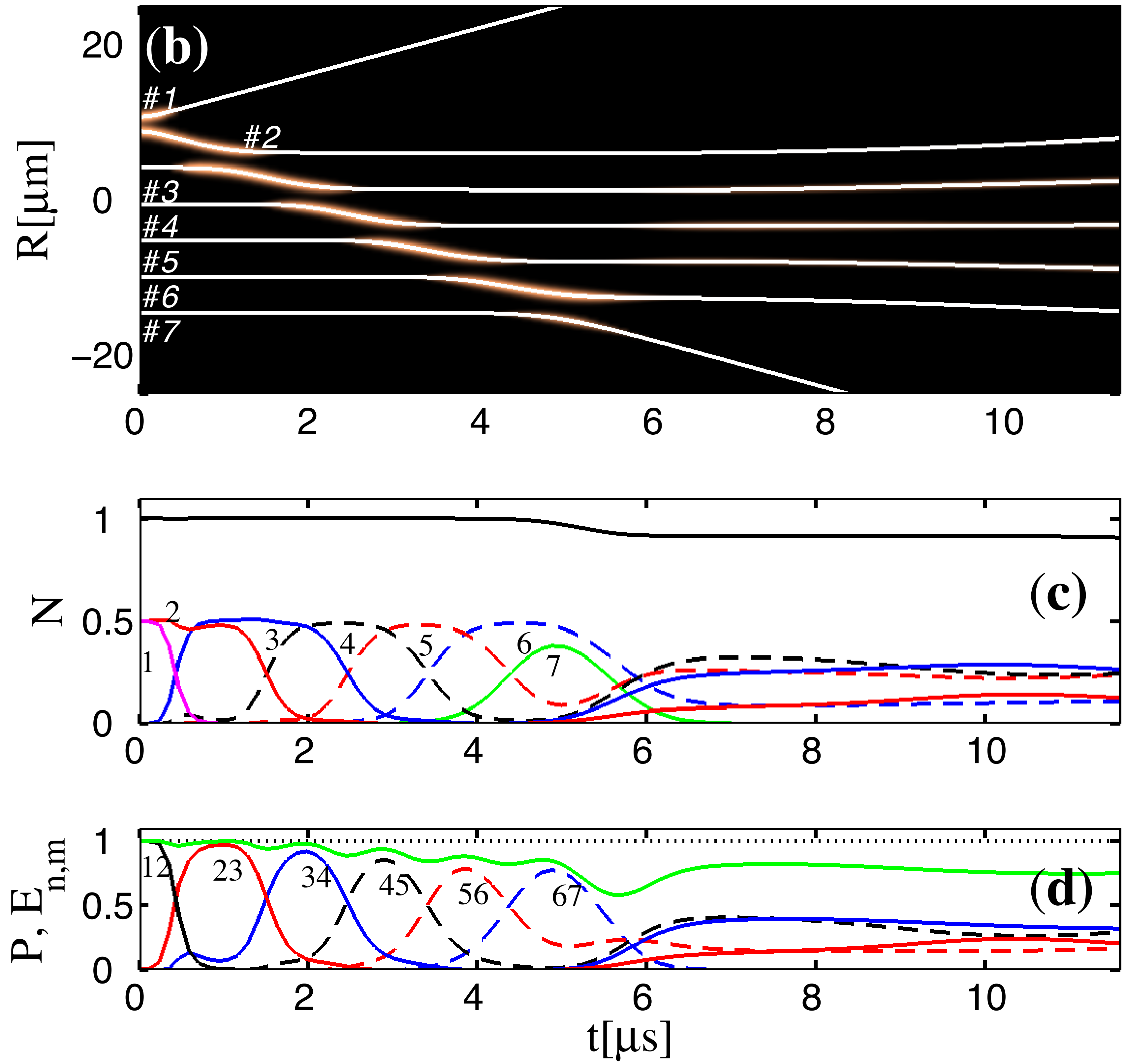


Entanglement transport

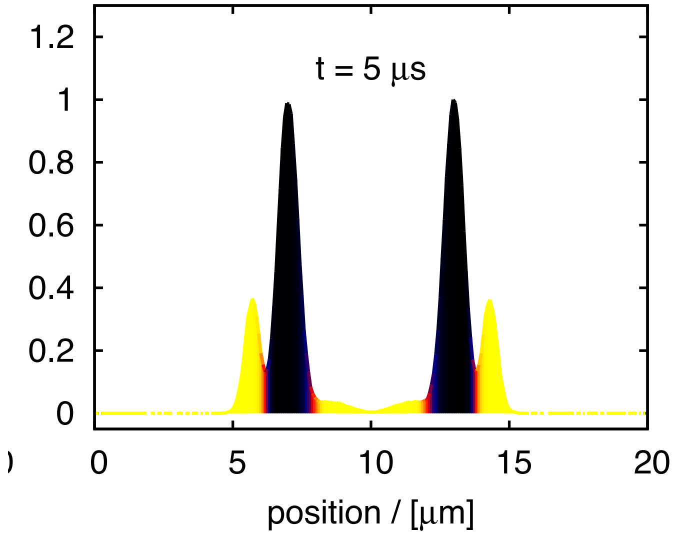
Mean positions
&
Mean excitation

population on initial adiabatic surface and on individual atoms

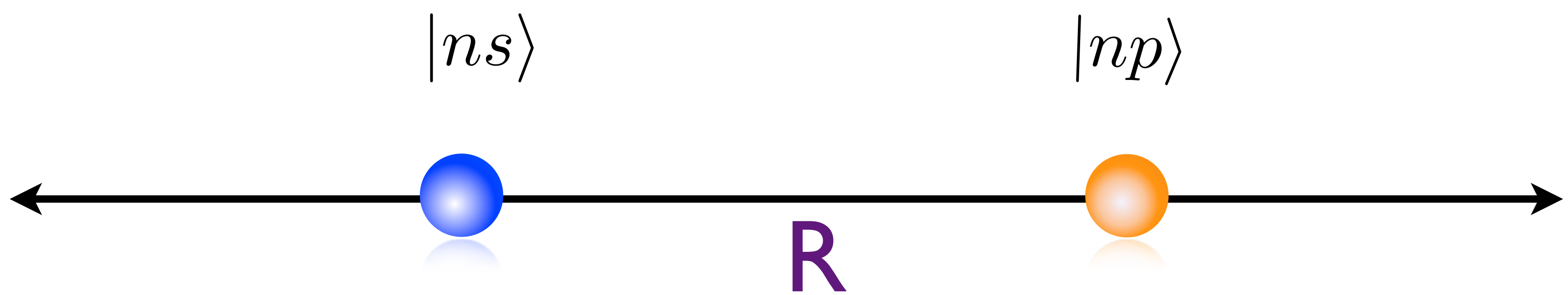
Entanglement between neighbors and Purity (-)



(4b) Entanglement between position and quantum state

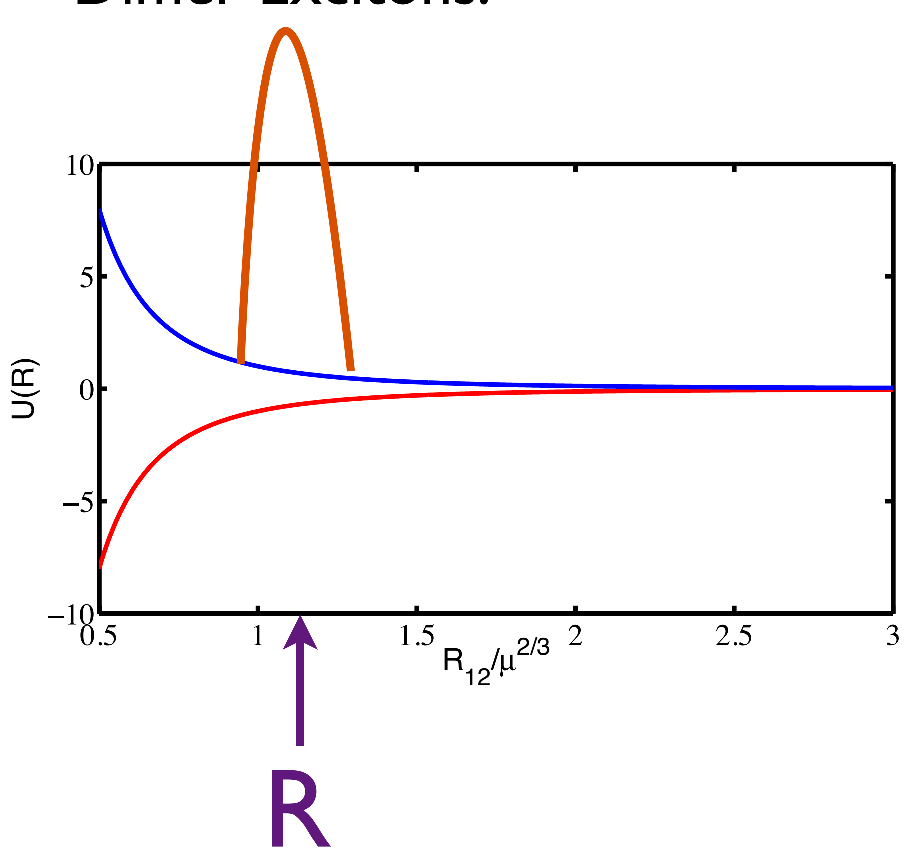


Entanglement generation



$$|\,sp\,\rangle = (|\,\varphi_1\,\rangle + |\,\varphi_2\,\rangle)/\sqrt{2}$$

Dimer Excitons:



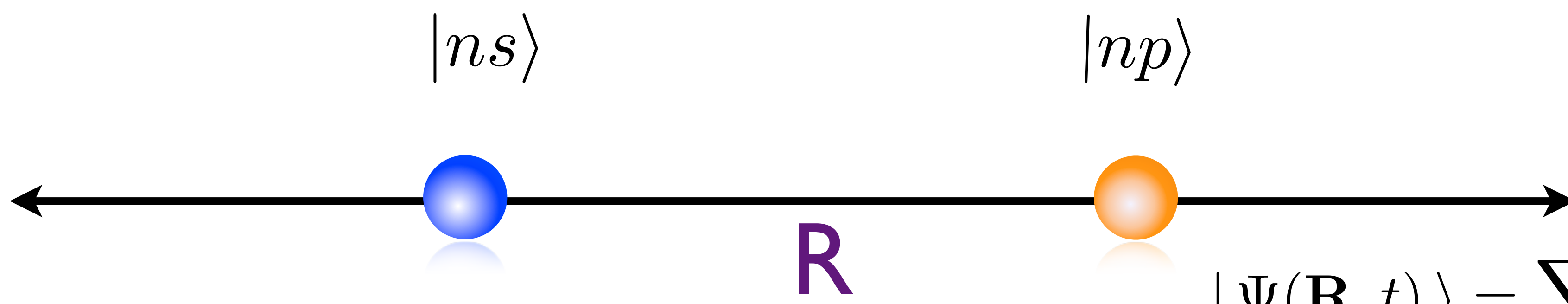
"attractive" eigenstate (exciton)

$$|\varphi_1\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle + |ps\rangle\right)$$

"repulsive" eigenstate (exciton)

$$|\varphi_2\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle - |ps\rangle\right)$$

Entanglement generation

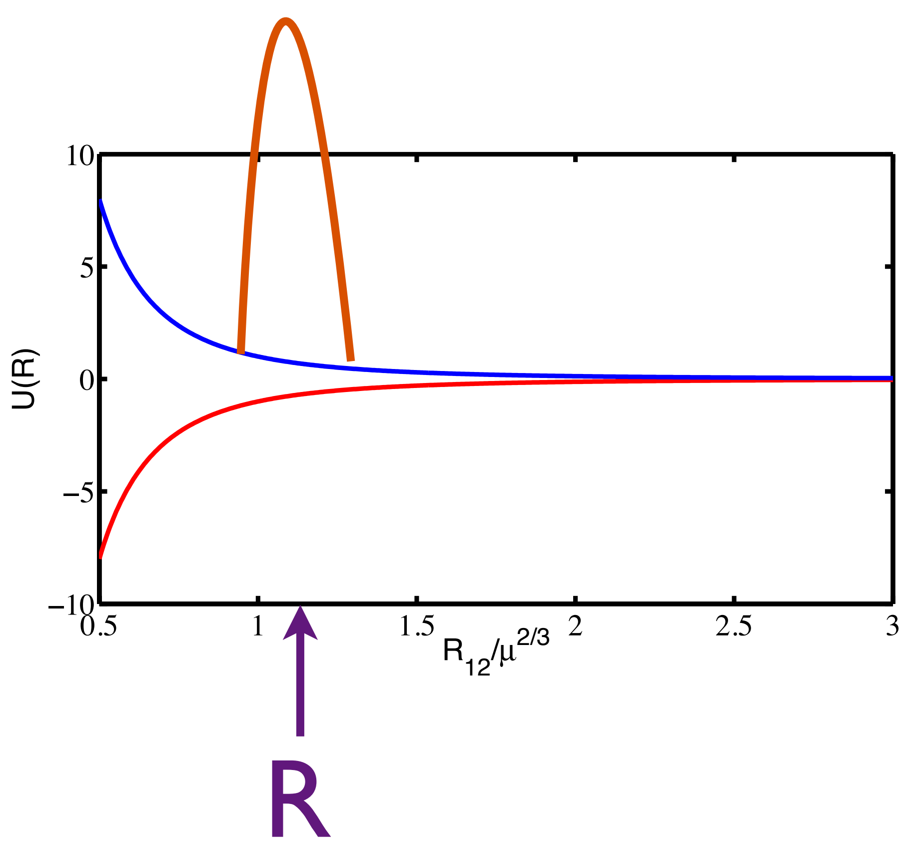


$$|\,\Psi(\mathbf{R},t)\,\rangle = \sum_n \phi_n(\mathbf{R},t)|\,\varphi_n(t)\,\rangle$$

$$|\,sp\,\rangle = (|\,\varphi_1\,\rangle + |\,\varphi_2\,\rangle)/\sqrt{2}$$

$$\int dR|\phi_{1,2}(\mathbf{R})|^2 = \frac{1}{2}$$

Dimer Excitons:



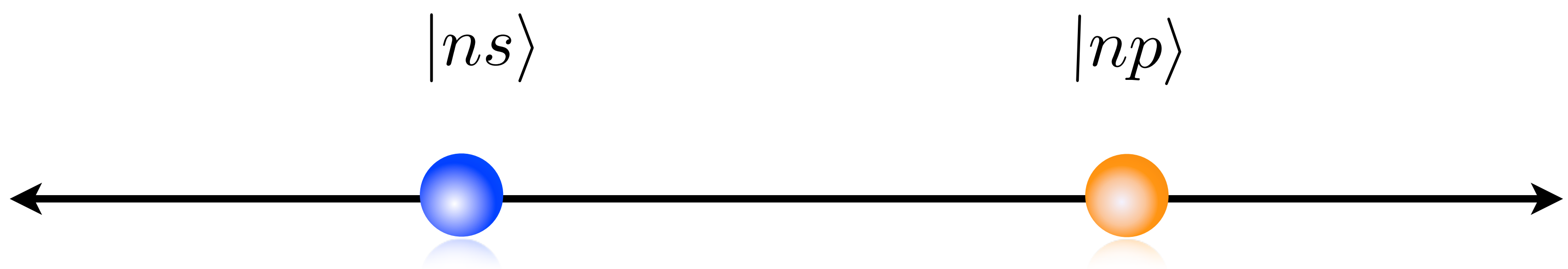
“attractive” eigenstate (exciton)

$$|\varphi_1\rangle = \frac{1}{\sqrt{2}}(|sp\rangle + |ps\rangle)$$

“repulsive” eigenstate (exciton)

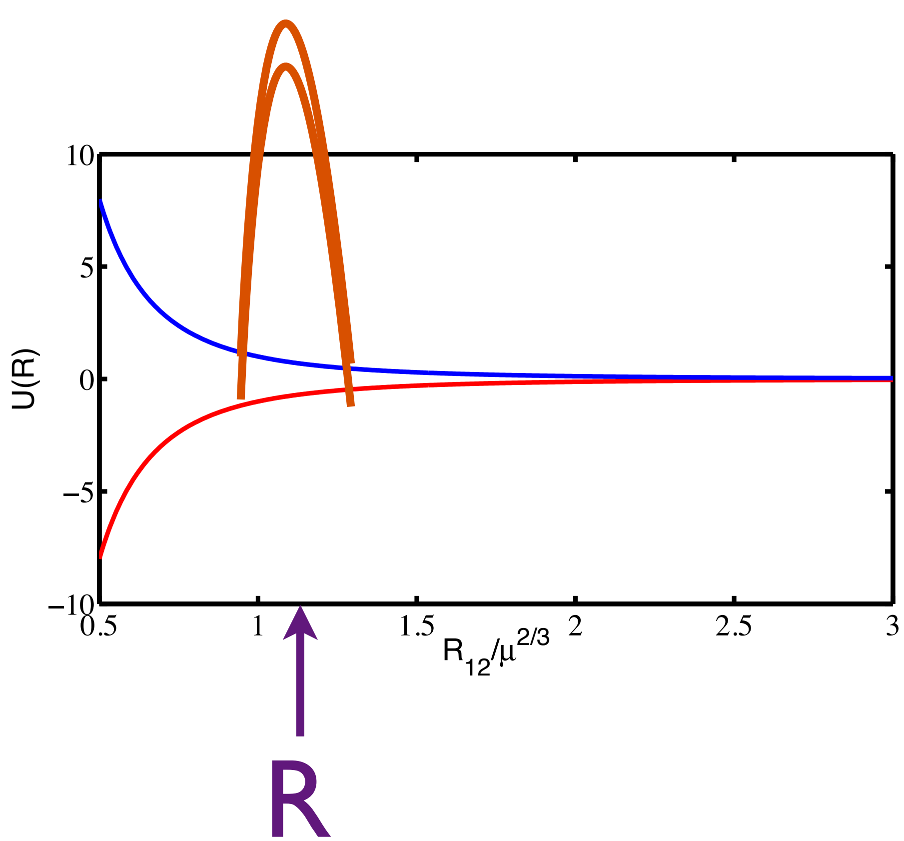
$$|\varphi_2\rangle = \frac{1}{\sqrt{2}}(|sp\rangle - |ps\rangle)$$

Entanglement generation



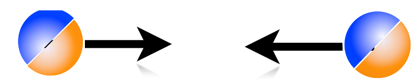
$$|\,sp\,\rangle = (|\,\varphi_1\,\rangle + |\,\varphi_2\,\rangle)/\sqrt{2}$$

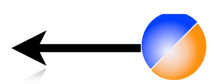
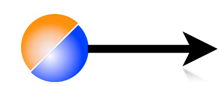
Dimer Excitons:



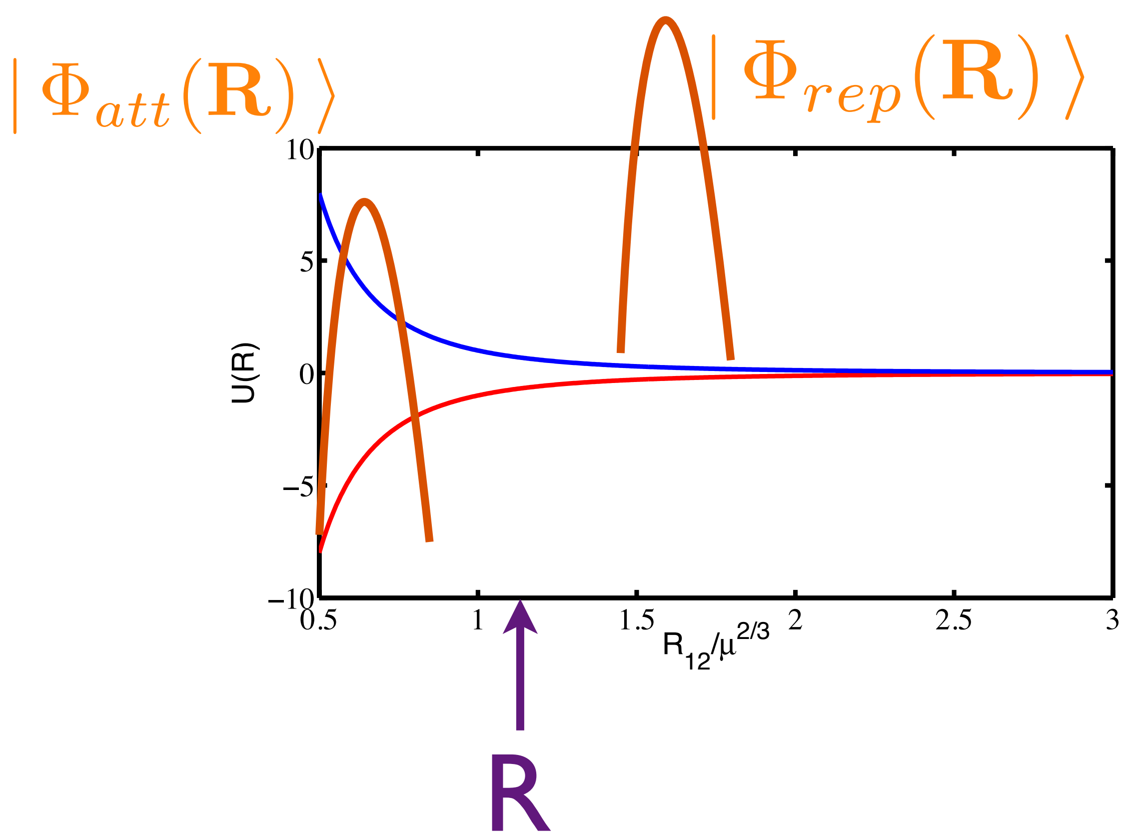
Entanglement generation

$$|\varphi_1\rangle = \frac{1}{\sqrt{2}}(|sp\rangle + |ps\rangle)$$



 $$|\varphi_2\rangle = \frac{1}{\sqrt{2}}(|sp\rangle - |ps\rangle)$$ 

Dimer Excitons:



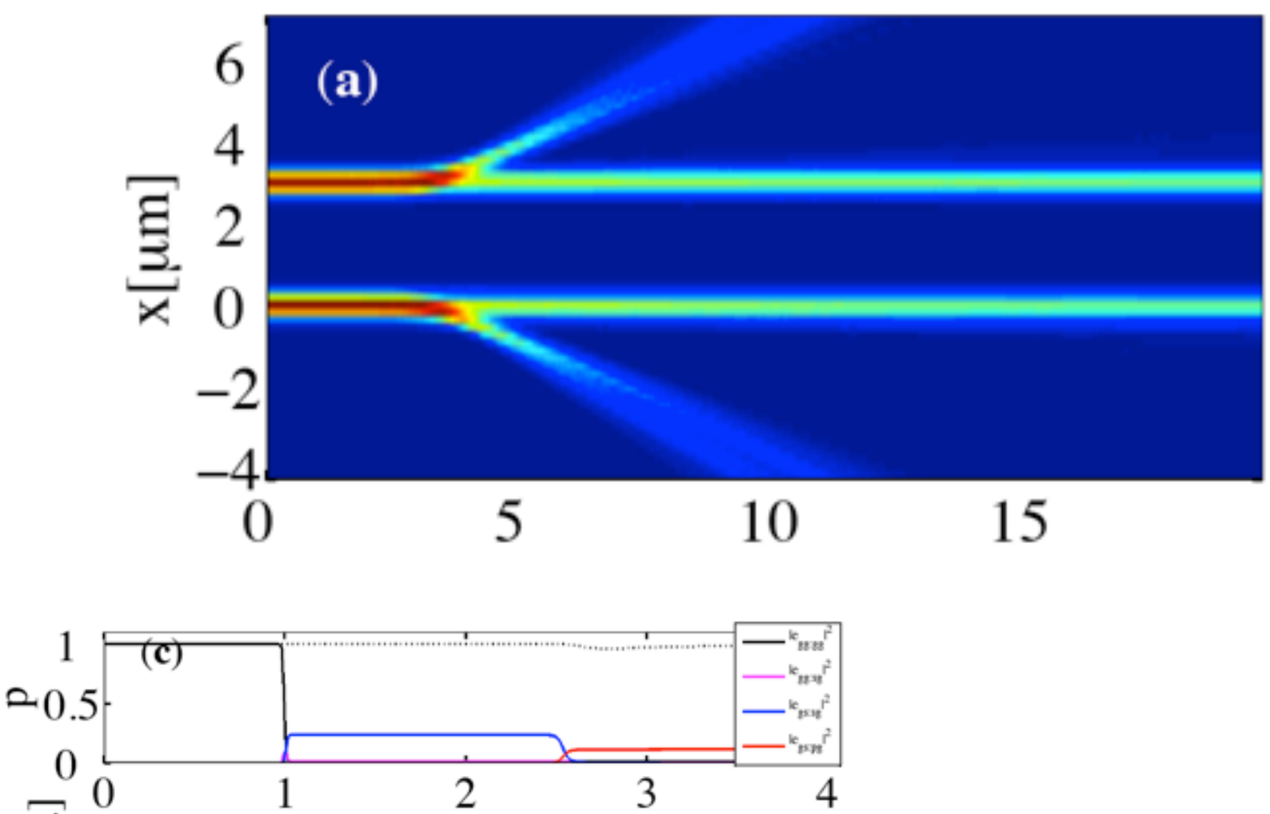
State after some acceleration phase

$$\Psi = \frac{1}{\sqrt{2}}(|\Phi_{rep}(\mathbf{R})\rangle|\varphi_2\rangle + |\Phi_{att}(\mathbf{R})\rangle|\varphi_1\rangle)$$

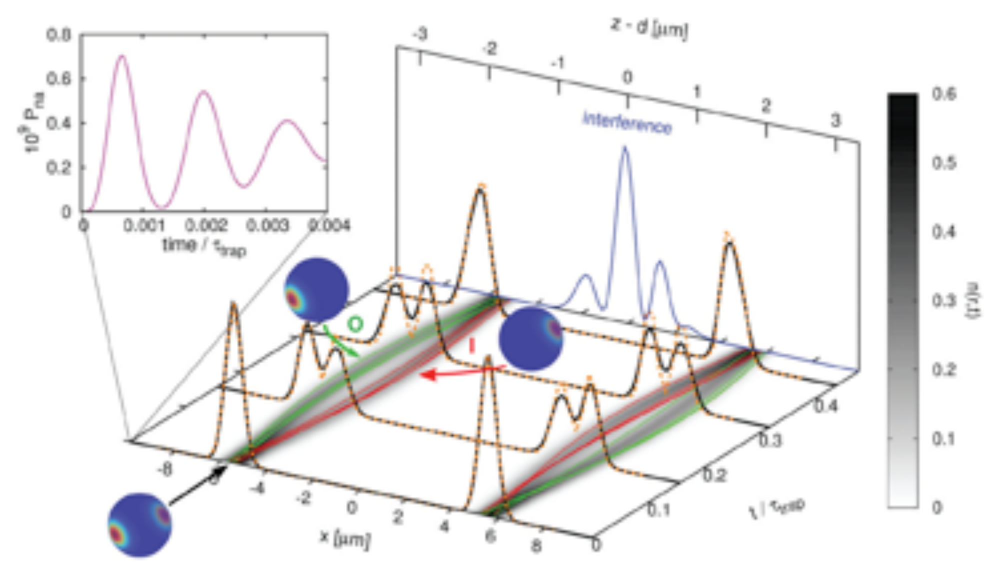
Entanglement between state and position, multi BO-surface dynamics

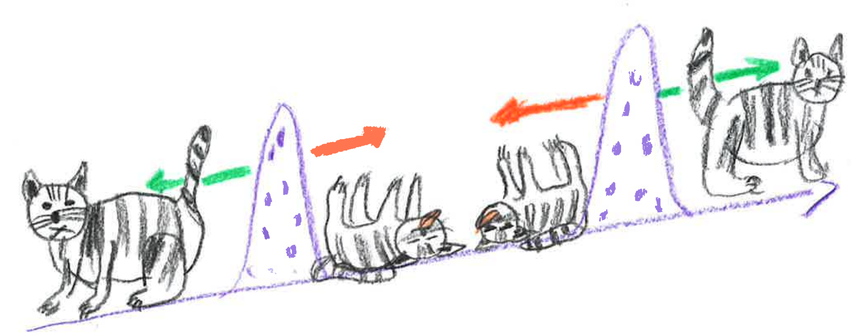
Entanglement generation

Pulsed source of EPR entangled atoms



Optically resolvable Schrödinger's cat state





Workshop poster

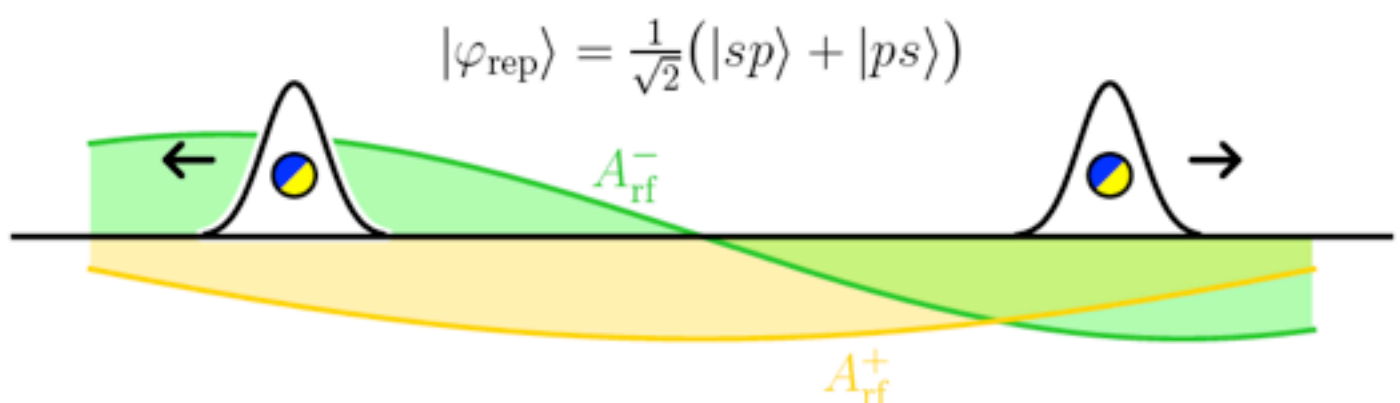
"Entangled Rydberg atom pairs on demand",

by Michael Genkin

Workshop talk,

next TUE, 11:30

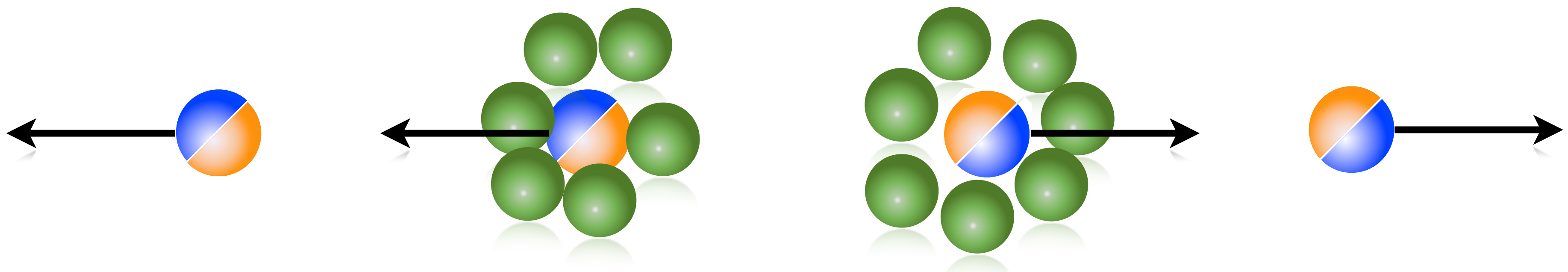
(4c) Entanglement detection



Rydberg pair source

*e.g. H. Park, E. S. Shuman, and T. F. Gallagher, Phys. Rev. A **84** 052708 (2011).*

Periodic generation of repulsive excitons

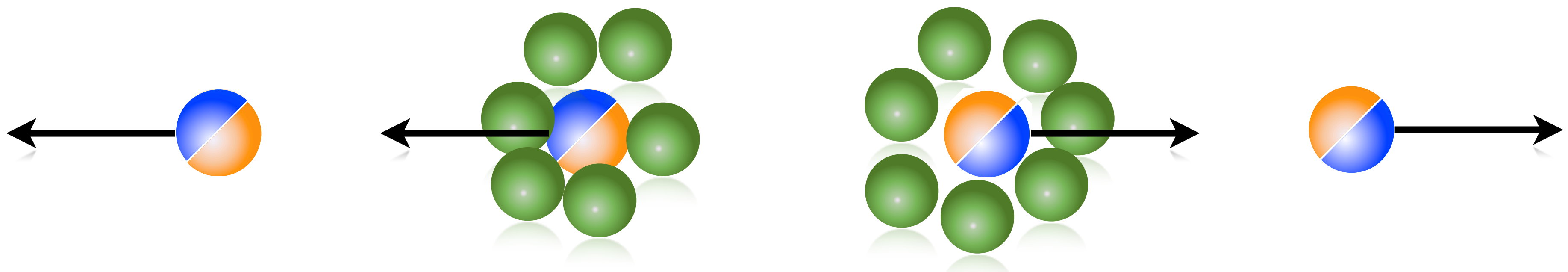


Bell-state $$|\varphi_2\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle + |ps\rangle\right)$$

Einstein-Podolsky-Rosen scenario

Rydberg

Periodic generation of repulsive excitons

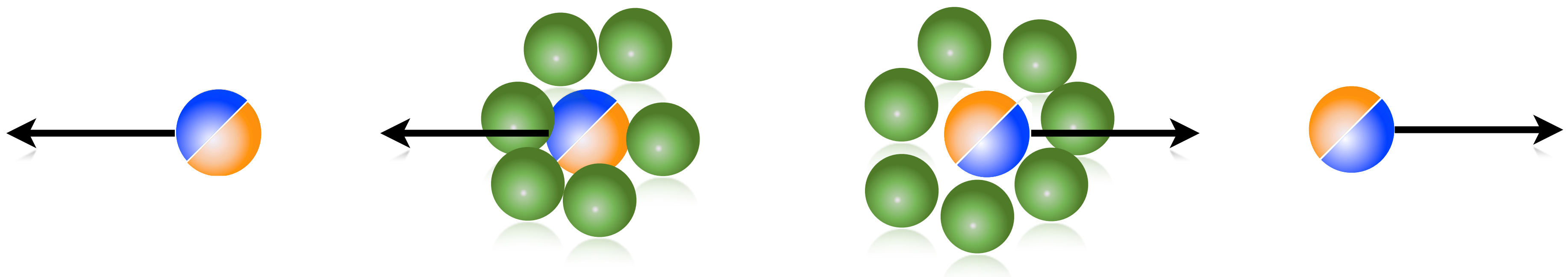


Bell-state $|\varphi_2\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle + |ps\rangle\right)$

Einstein-Podolsky-Rosen scenario

Rydberg

Periodic generation of repulsive excitons



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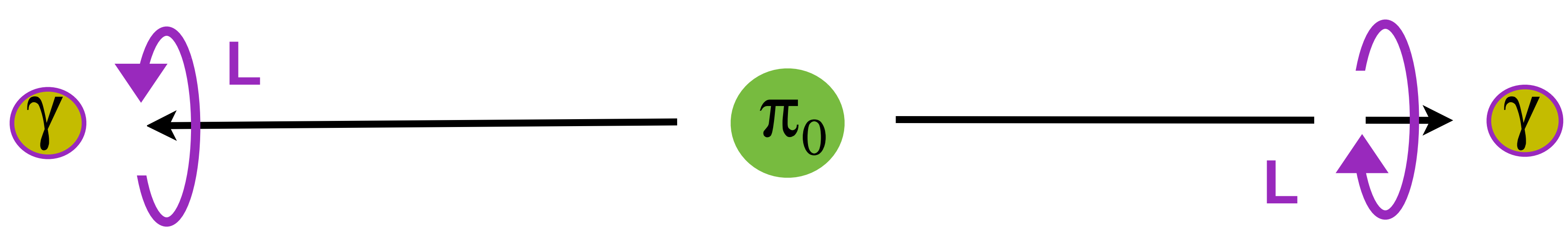
EPR-Scenario

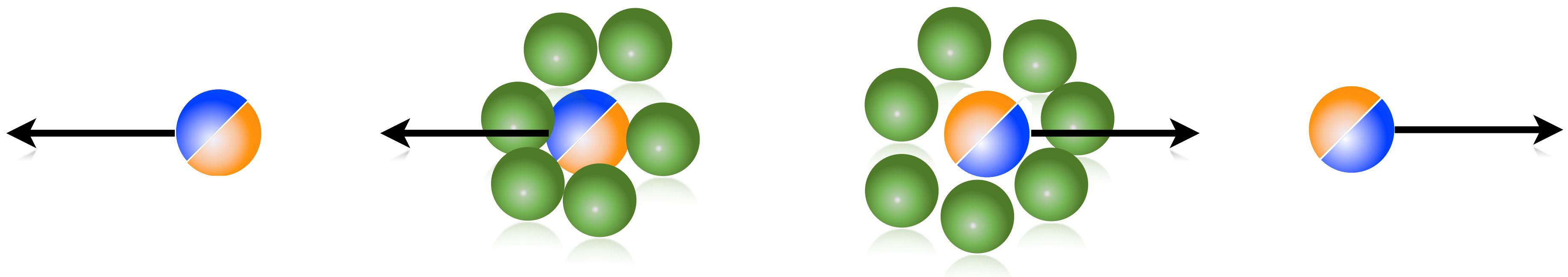


Bell-state $$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|LL\rangle - |RR\rangle\right)$$

Einstein-Podolsky-Rosen scenario

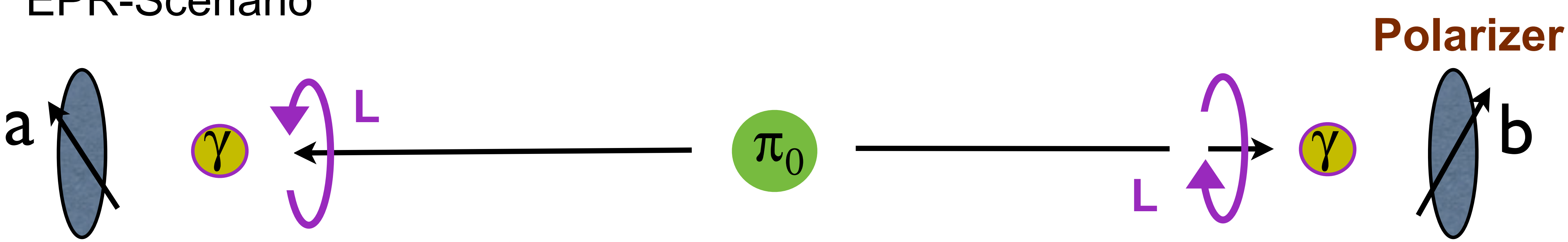
Rydberg

Periodic generation of repulsive excitons



Bell-state $|\varphi_2\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle + |ps\rangle\right)$

EPR-Scenario



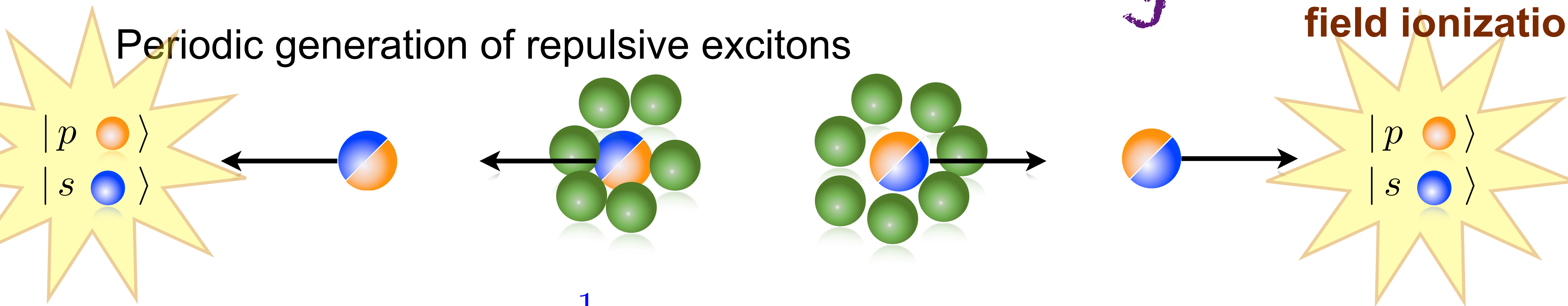
Bell-state $|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|LL\rangle - |RR\rangle\right)$

Einstein-Podolsky-Rosen scenario

Rydberg

state-selective field ionization

Periodic generation of repulsive excitons

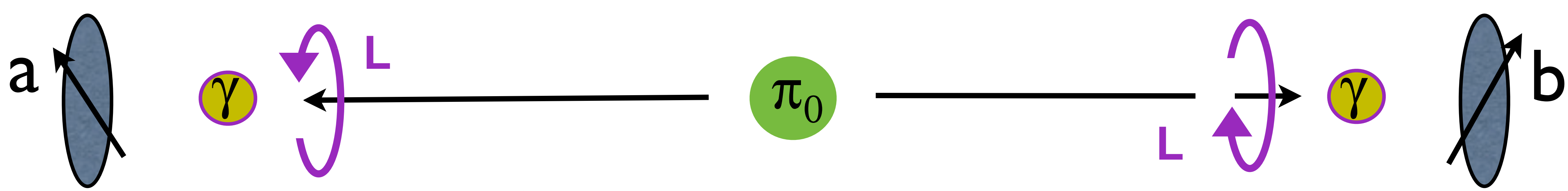


Bell-state

$$|\varphi_2\rangle = \frac{1}{\sqrt{2}}\left(|sp\rangle + |ps\rangle\right)$$

EPR-Scenario

Polarizer



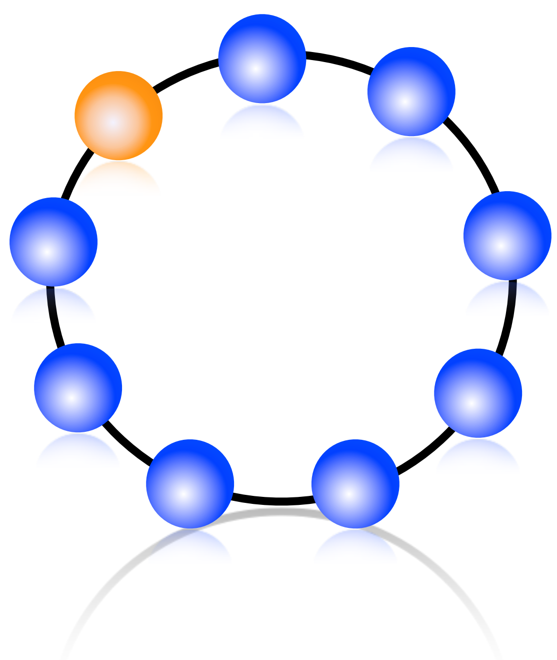
Bell-state

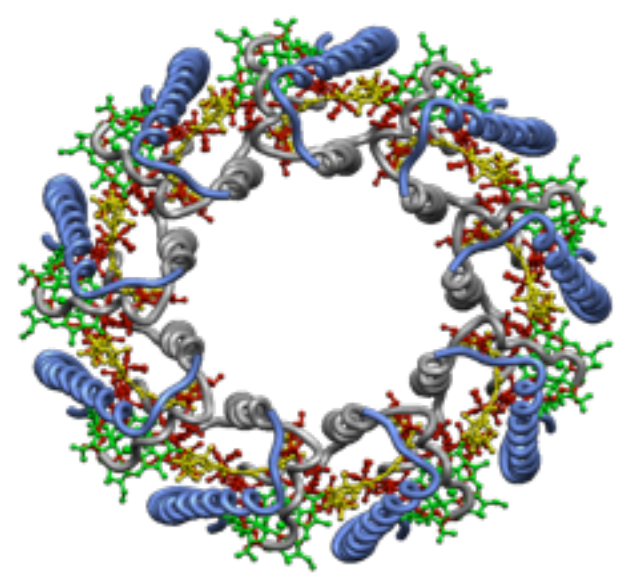
$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|LL\rangle - |RR\rangle\right)$$

mpipks
Finite Systems

MAX-PLANCK-GESELLSCHAFT

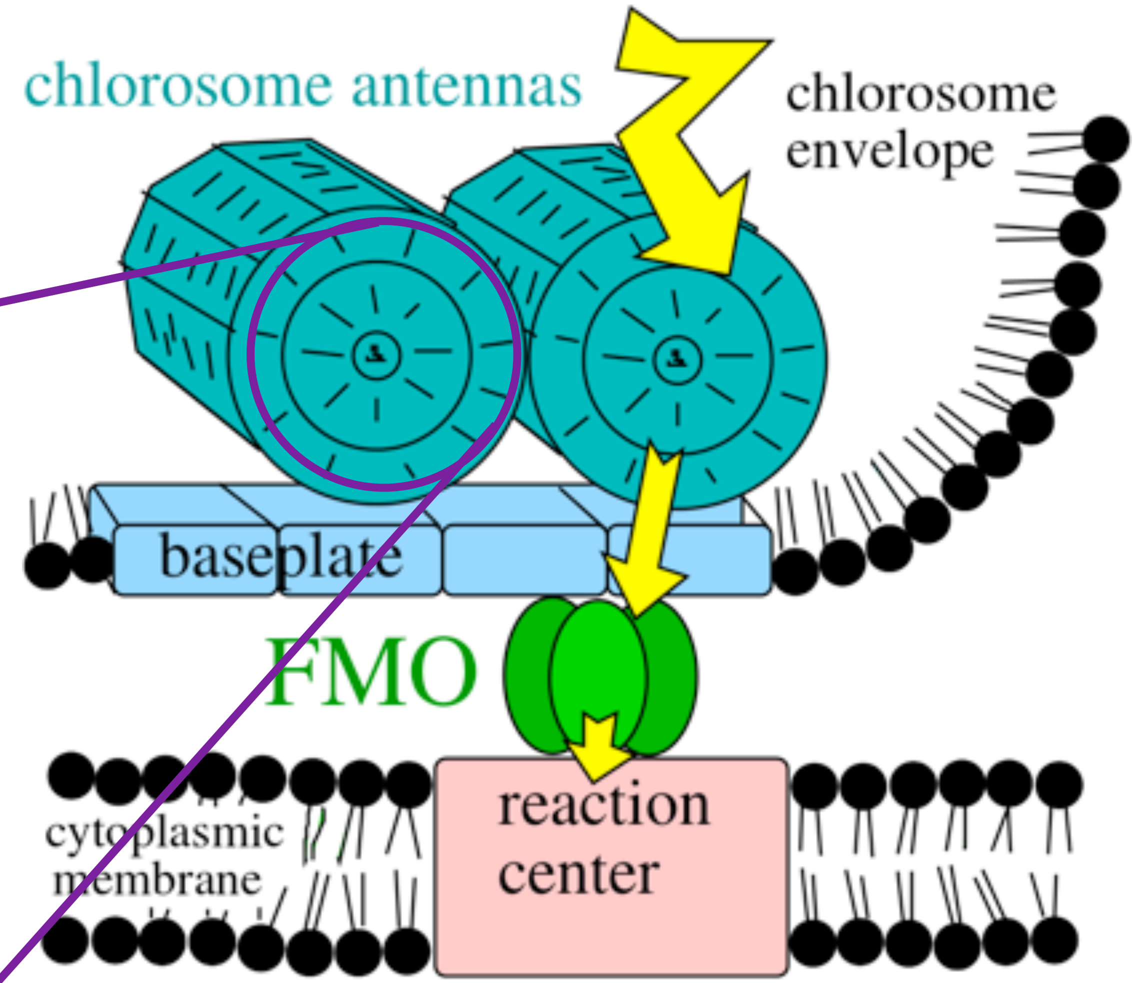
(5) Rydberg physics meets Biology





Photosynthetic light harvesting

- Light harvesting system of green sulphur bacteria



Light harvesting antenna

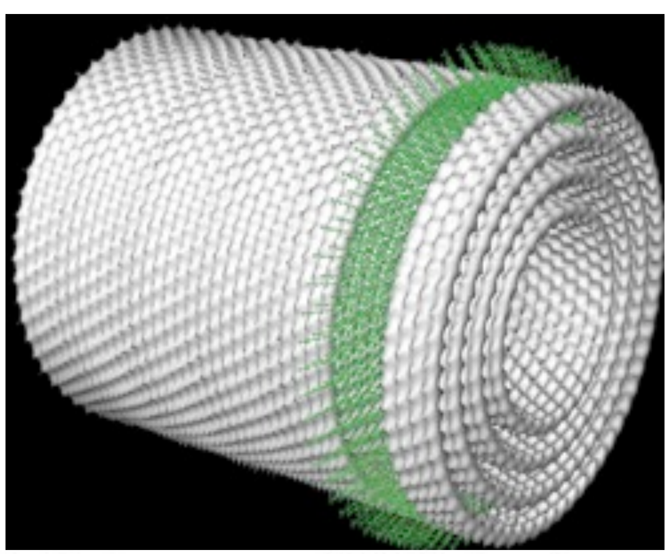
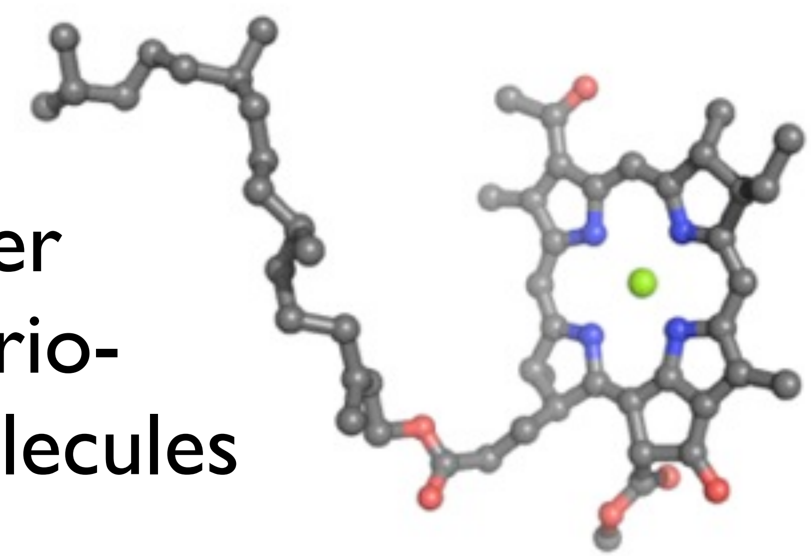


Bild: G. Oostergetel / Uni Groningen

- Consist of over 100000 bacterio-clorophyll molecules



Photosynthetic light harvesting

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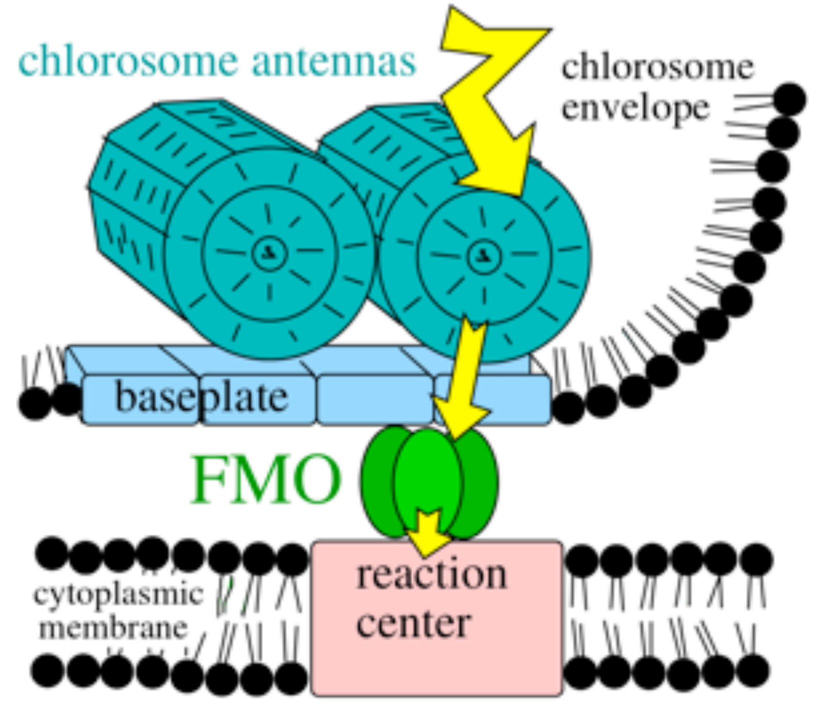


Light harvesting antenna

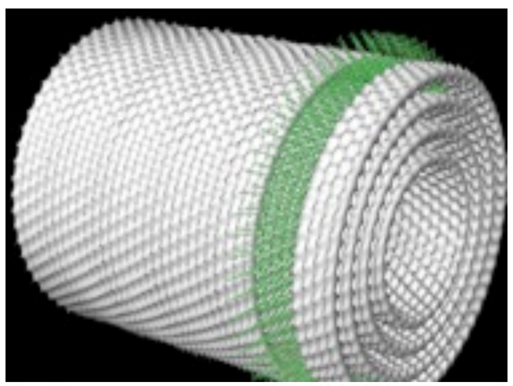
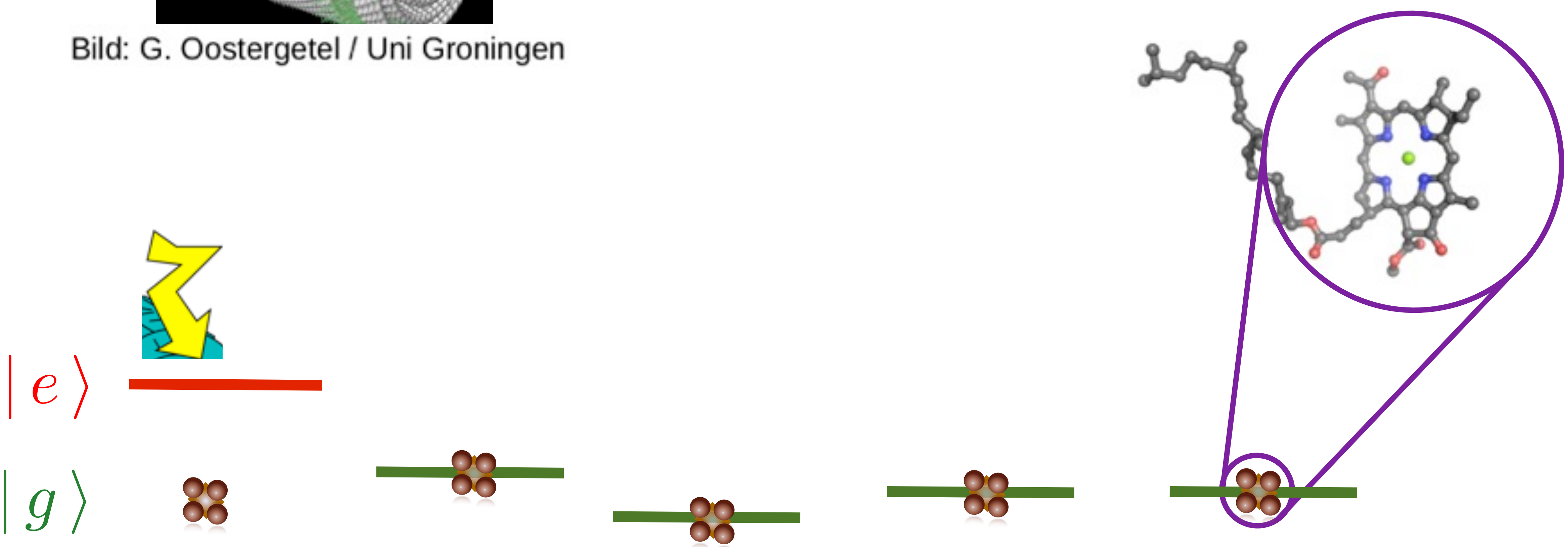
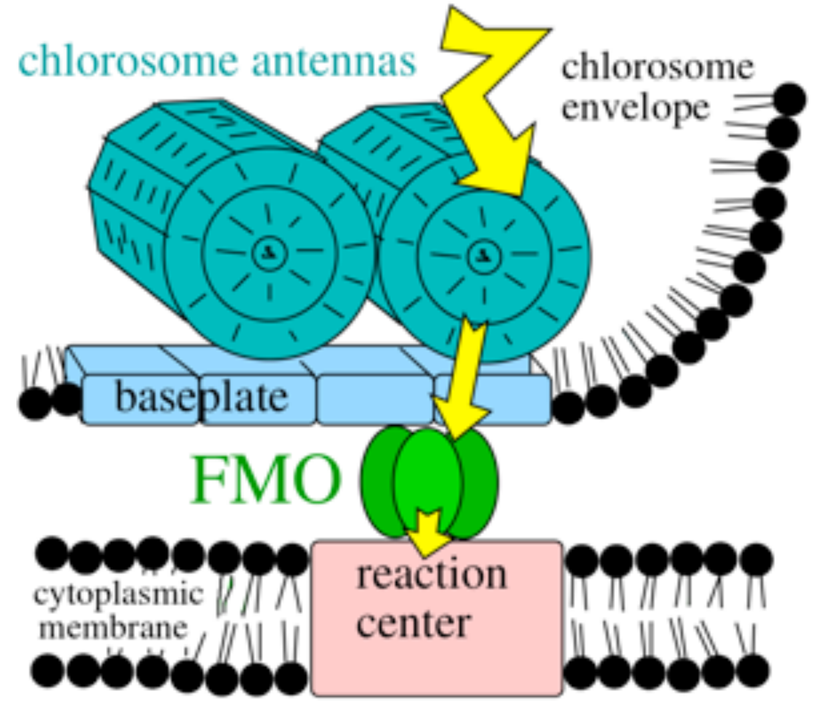


Bild: G. Oostergetel / Uni Groningen



Photosynthetic light harvesting

- Light harvesting system of green sulphur bacteria



Light harvesting antenna

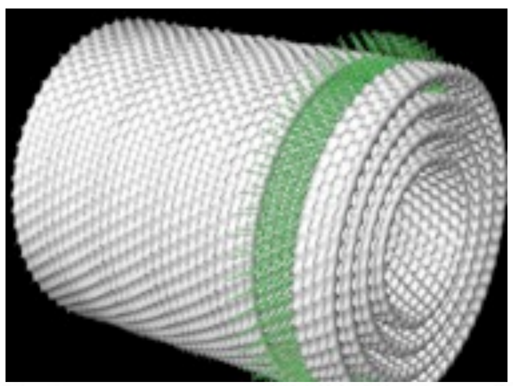
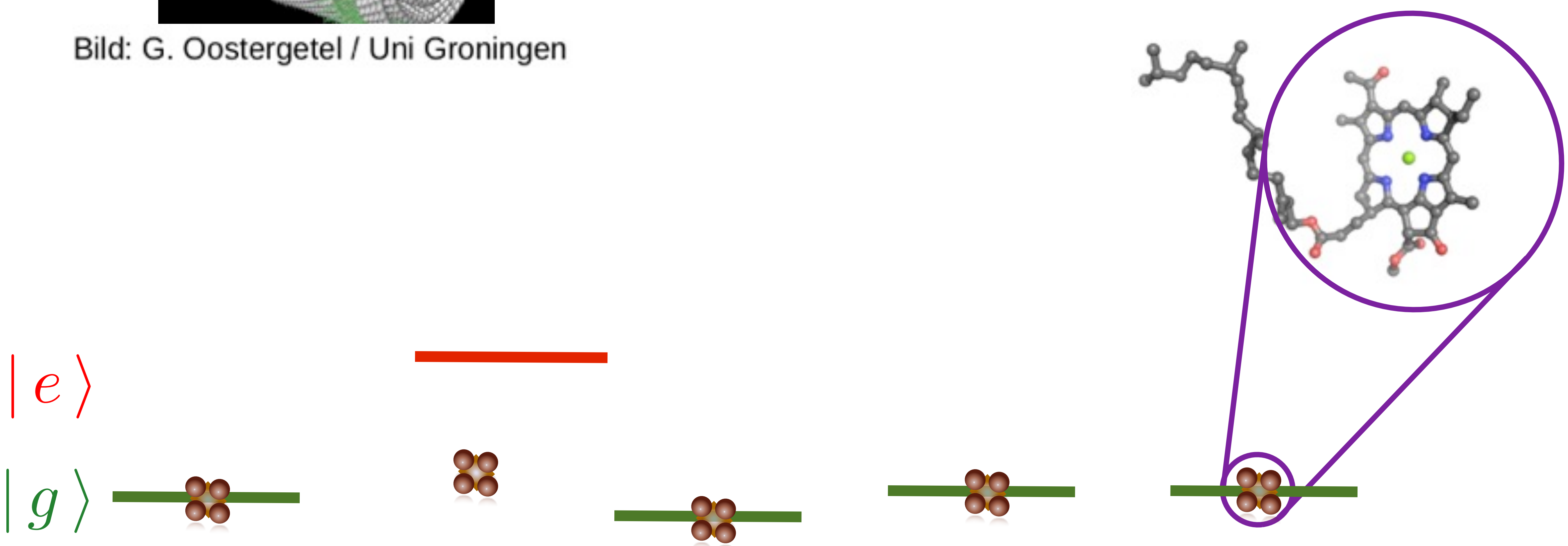


Bild: G. Oostergetel / Uni Groningen



Photosynthetic light harvesting

- Light harvesting system of green sulphur bacteria

Light harvesting antenna

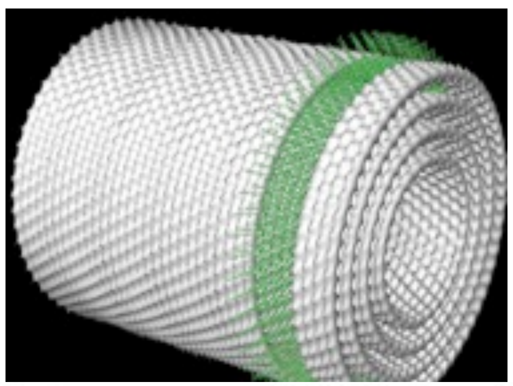
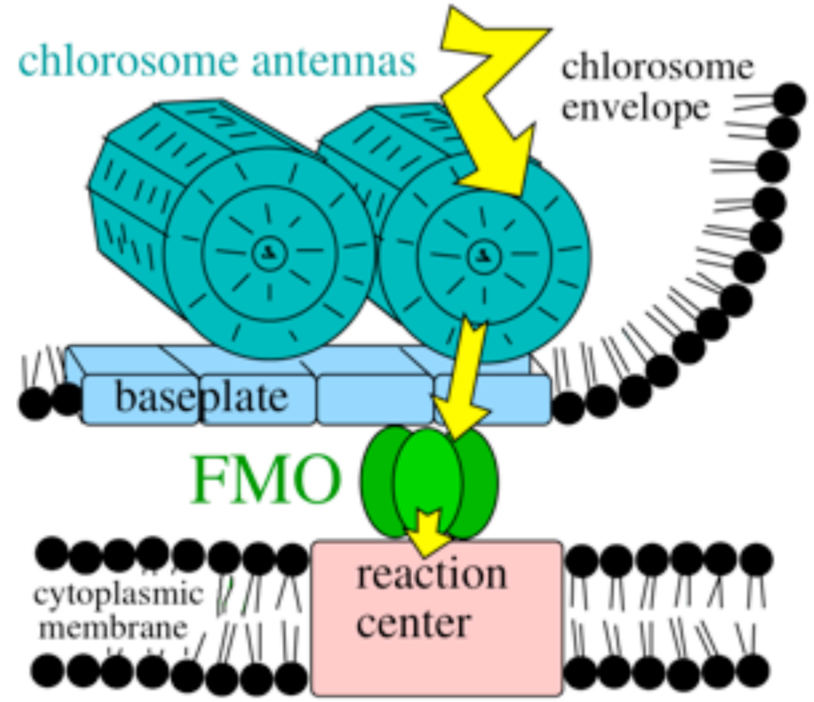
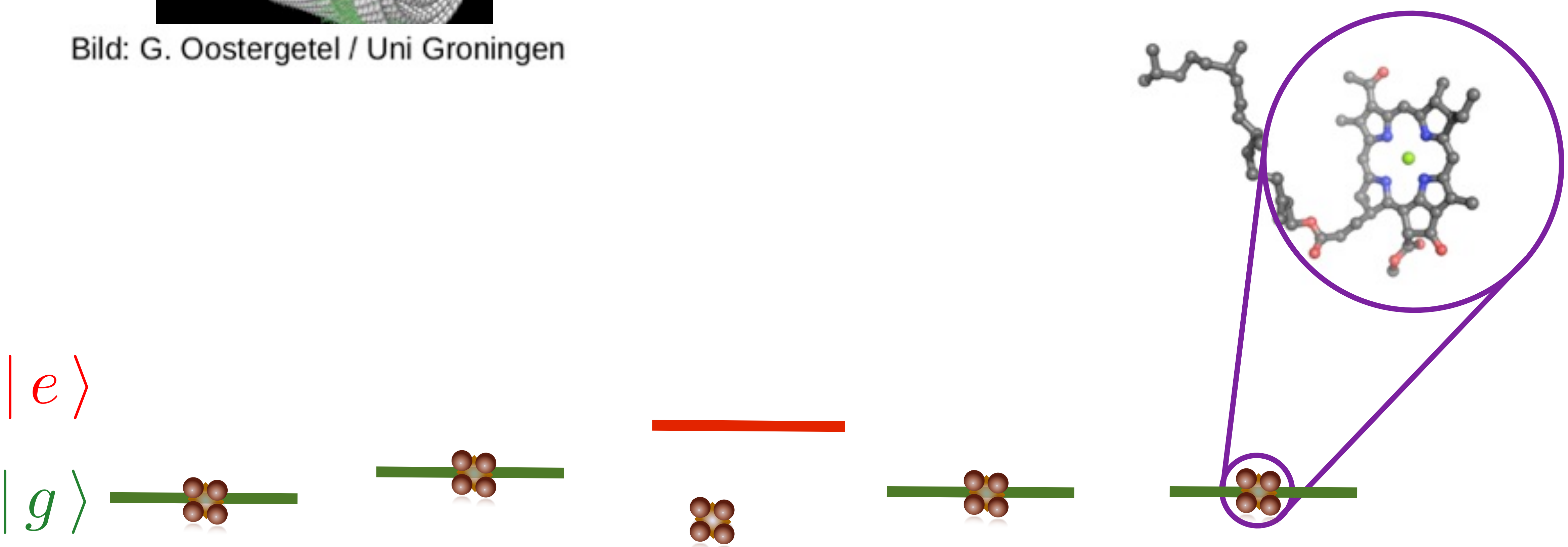


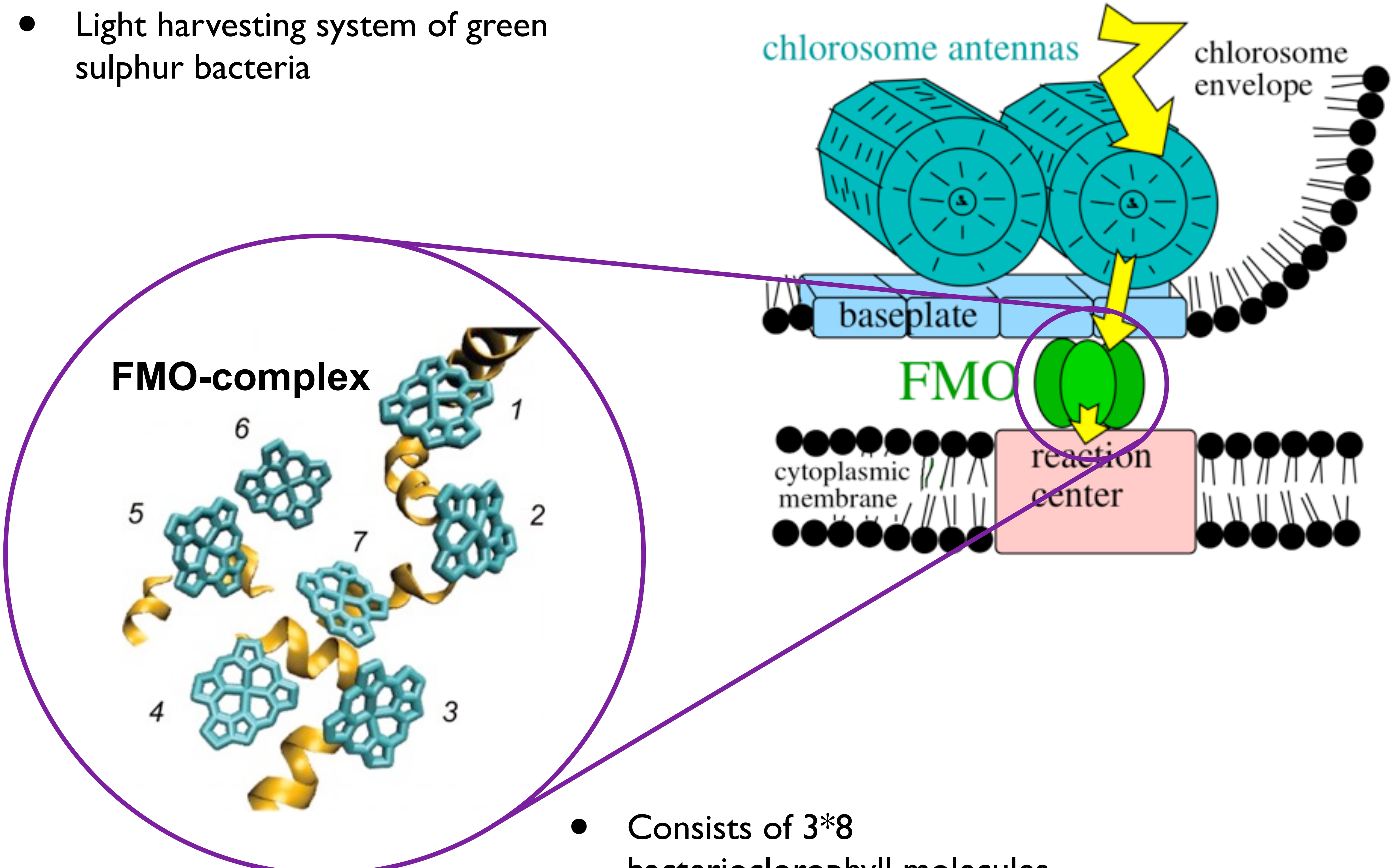
Bild: G. Oostergetel / Uni Groningen





Photosynthetic light harvesting

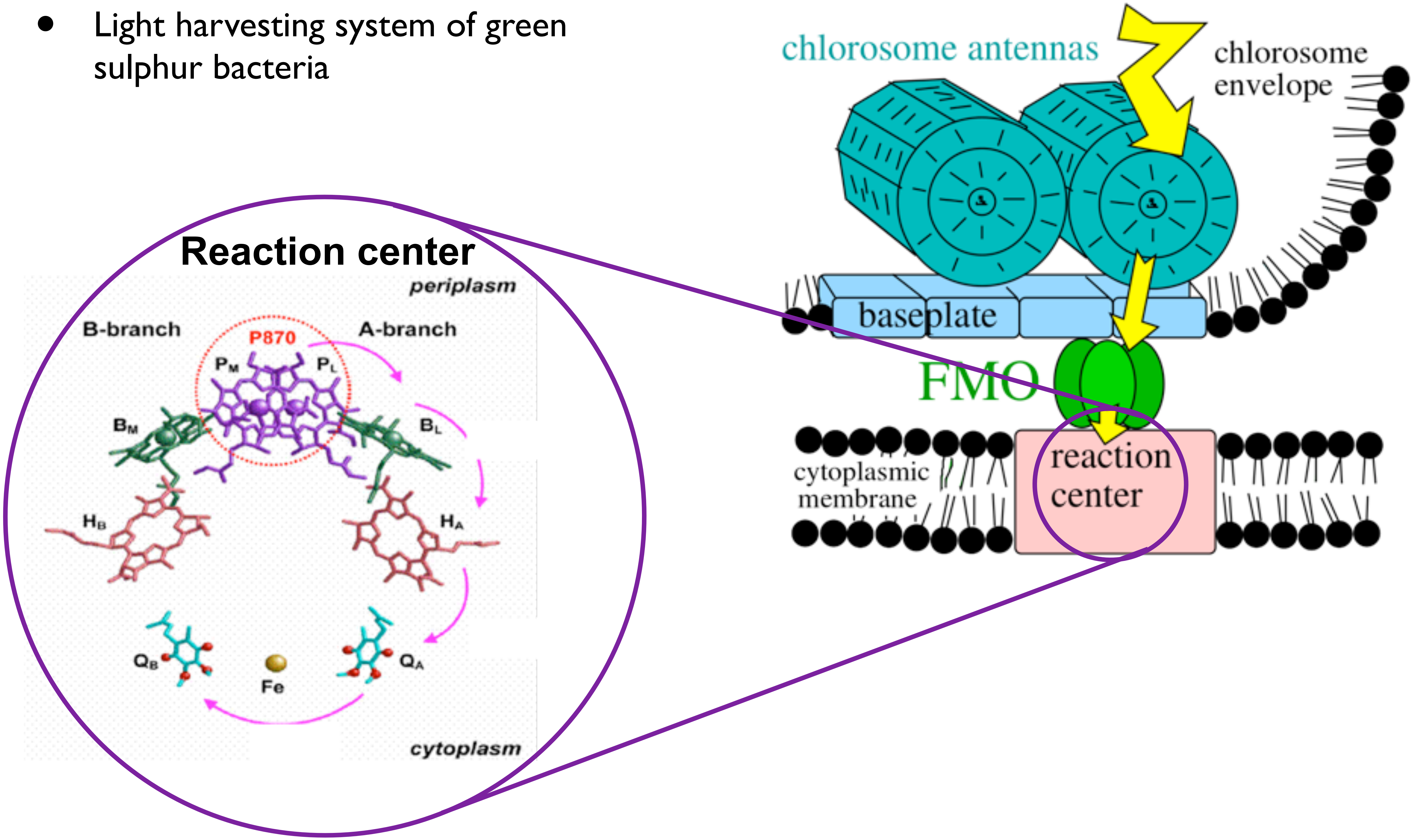
- Light harvesting system of green sulphur bacteria



- Consists of 3*8 bacterioclorophyll molecules

Photosynthetic light harvesting

- Light harvesting system of green sulphur bacteria



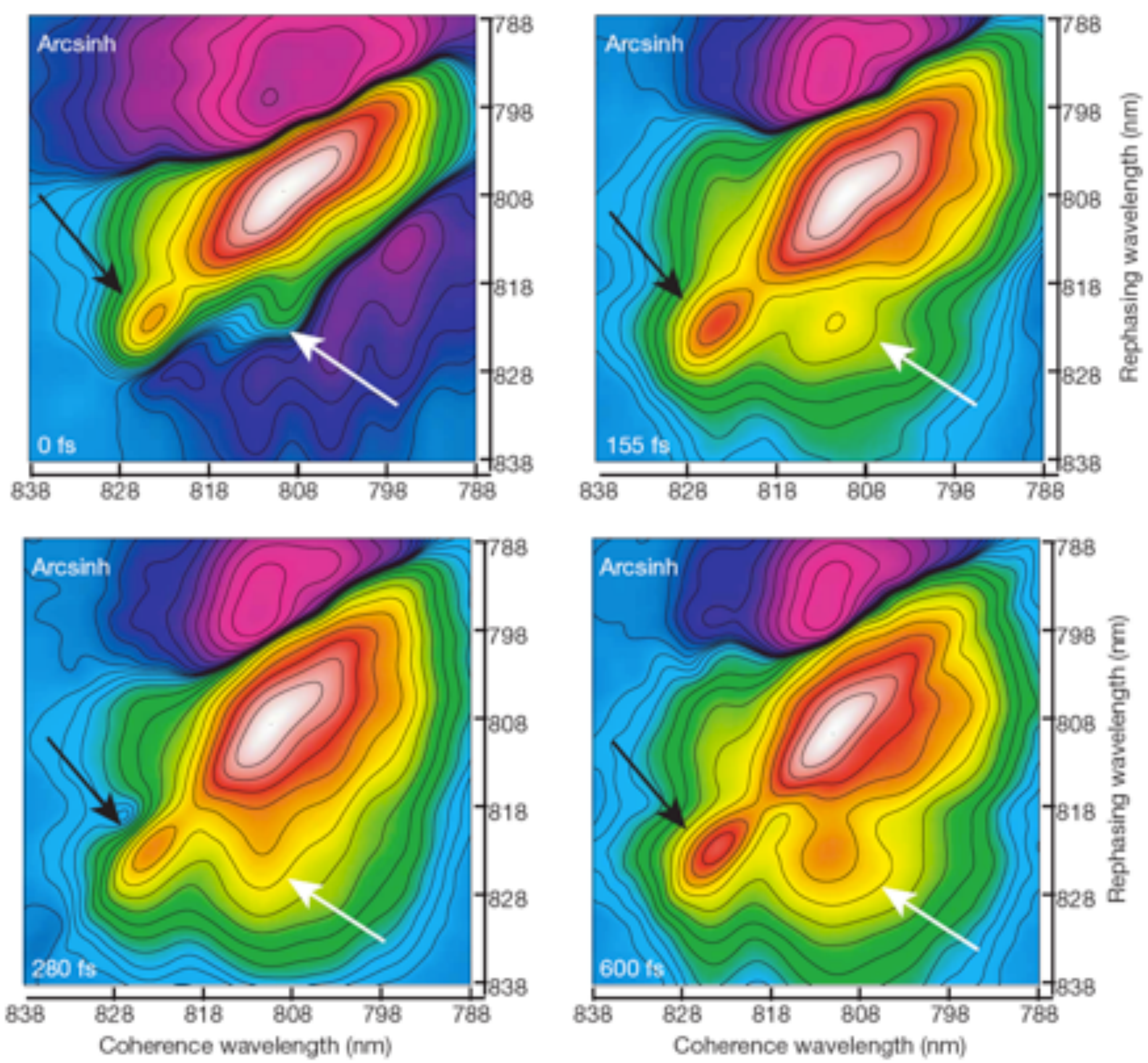
Quantum Biology (?)

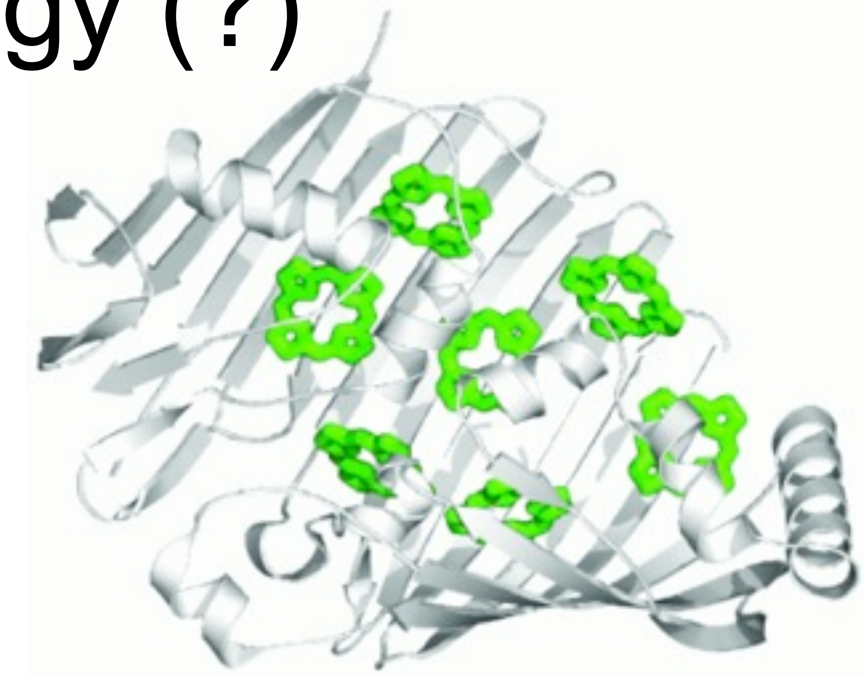
nature | Vol 446 | 12 April 2007 | doi:10.1038/nature05678

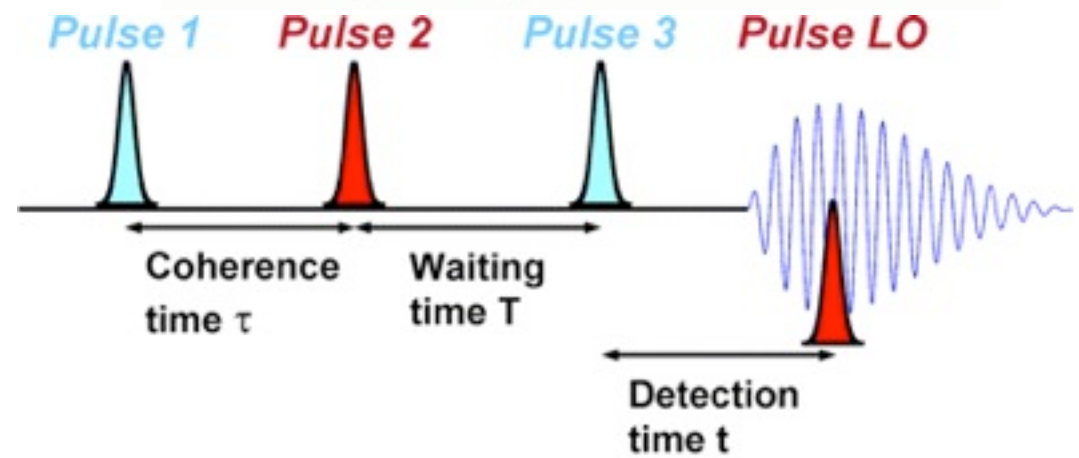
LETTERS

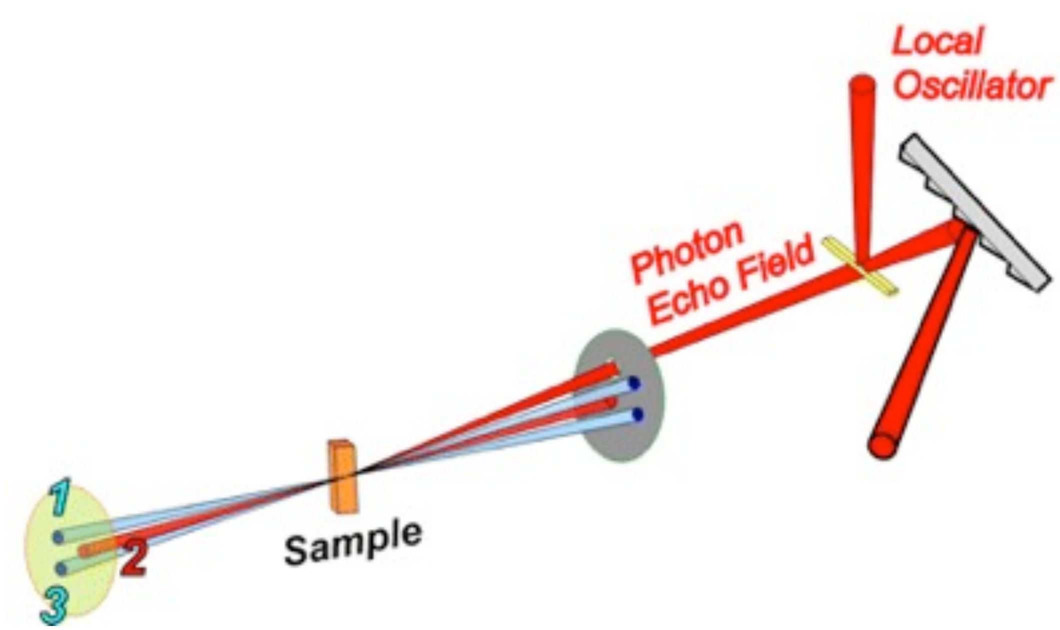
Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems

Gregory S. Engel[1,2], Tessa R. Calhoun[1,2], Elizabeth L. Read[1,2], Tae-Kyu Ahn[1,2], Tomáš Mančal[1,2]†, Yuan-Chung Cheng[1,2], Robert E. Blankenship[3,4] & Graham R. Fleming[1,2]







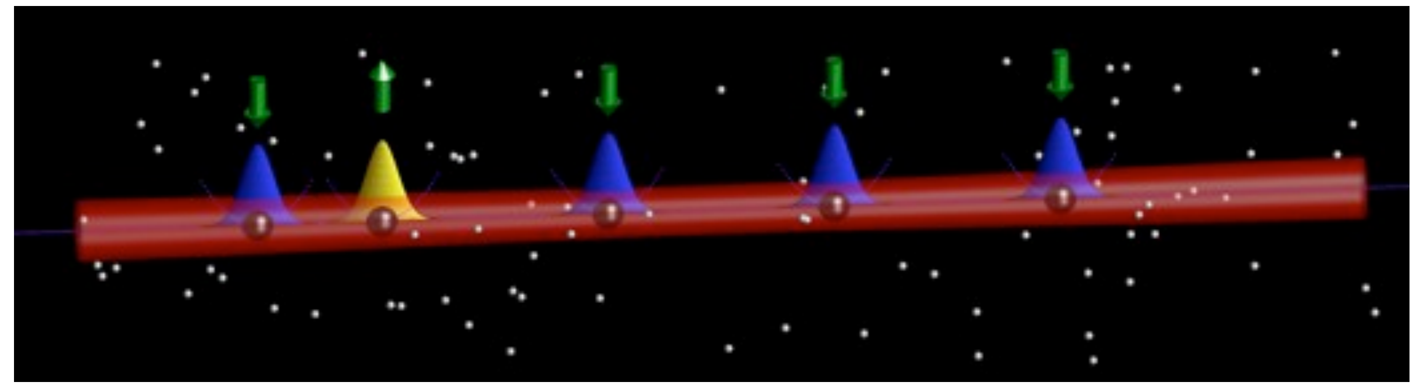


Tunable Rydberg aggregates

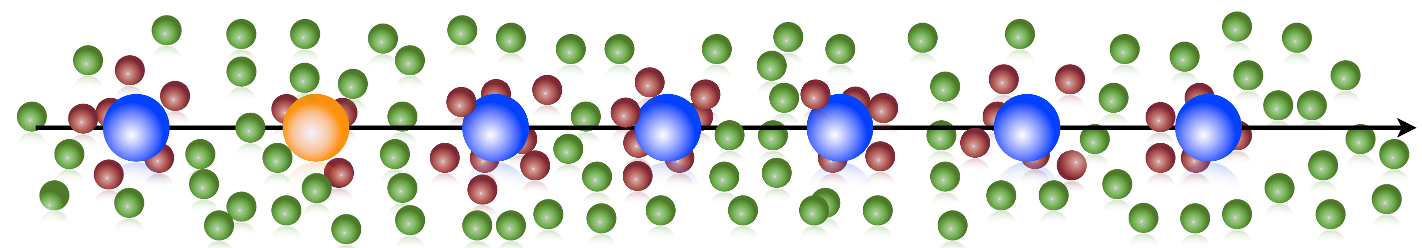
- Rydberg energy sink ("reaction centre")

O. Mülken, A. Blumen, T. Amthor, C. Giese, M. Reetz-Lamour and M. Weidemüller, *Phys. Rev. Lett.* ***99*** *090601 (2007)*

- Analog light harvesting system

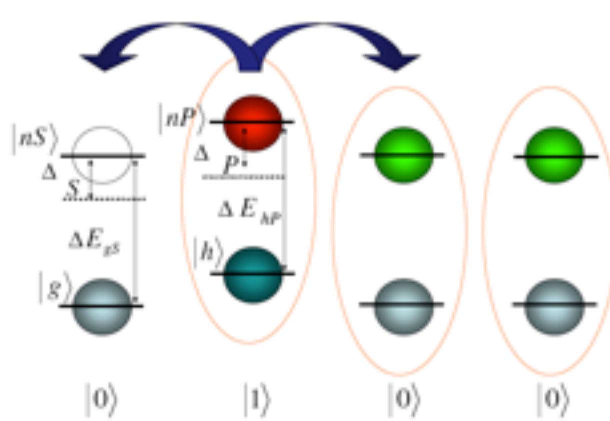


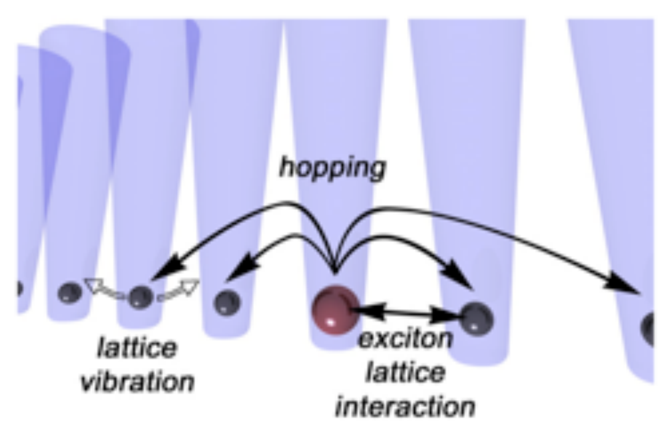
Interaction with background gas can create site energy disorder



- Analog Holstein model

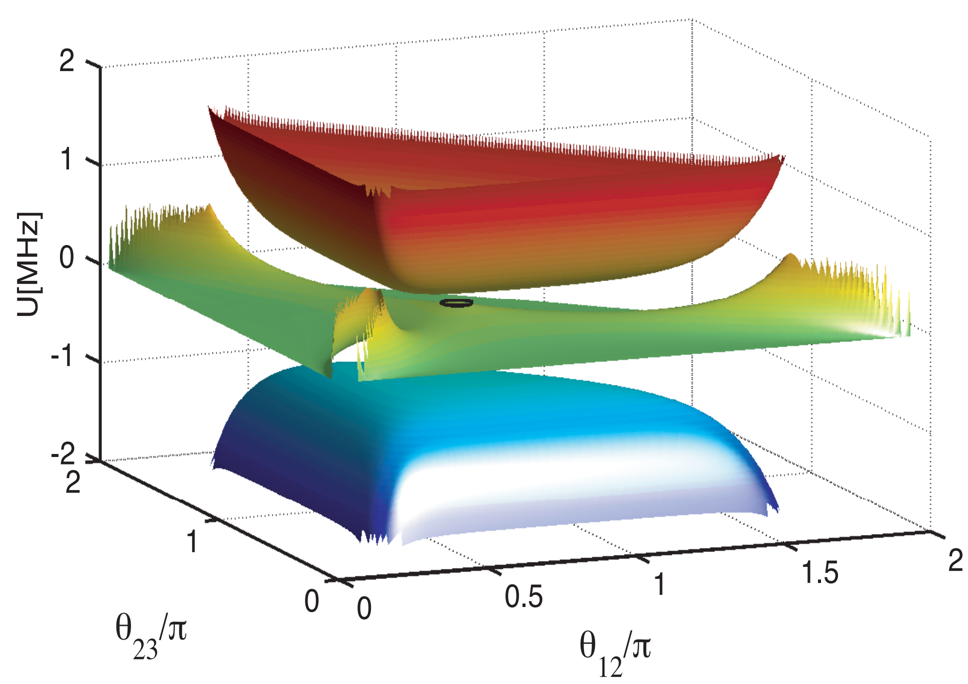
*J. P. Hague and C. MacCormick, New J. Phys., **14** 033019 (2012).*





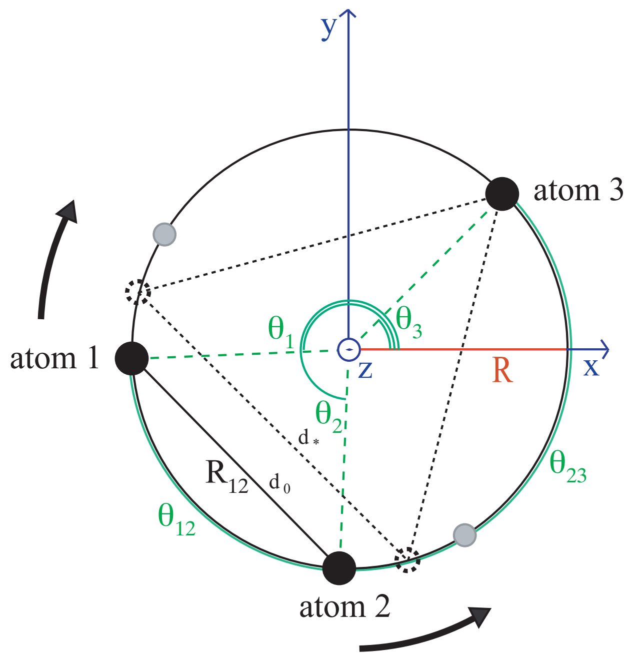
mpipks
Finite Systems

(6) Rydberg physics meets chemistry



Ring trimer

three atoms confined on ring



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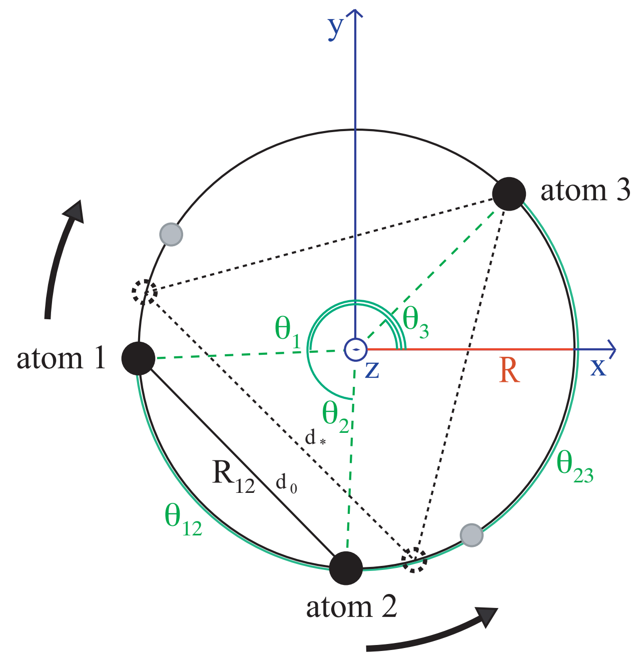
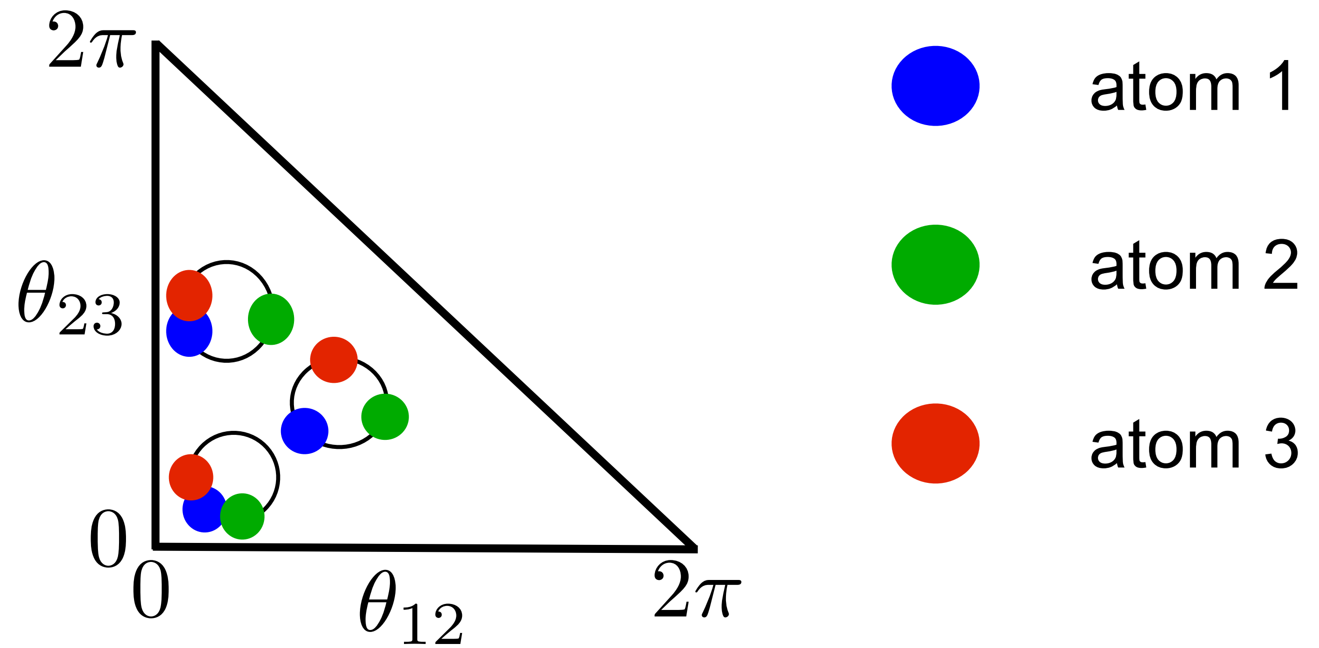


parameter space



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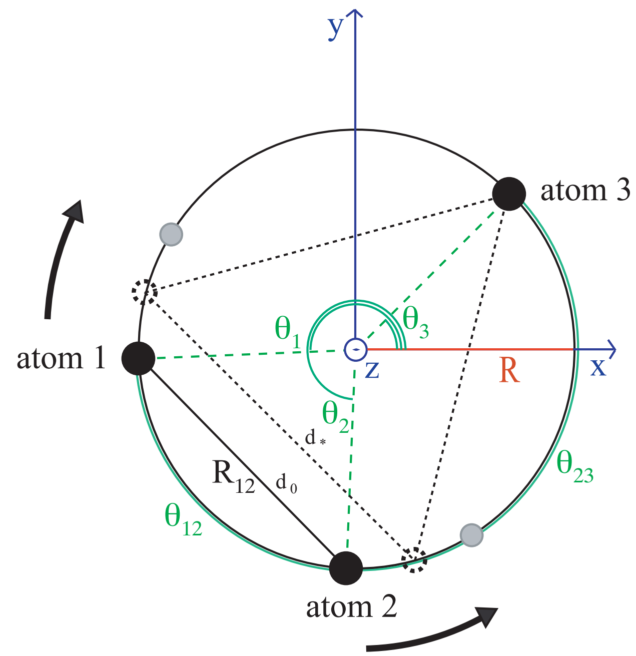

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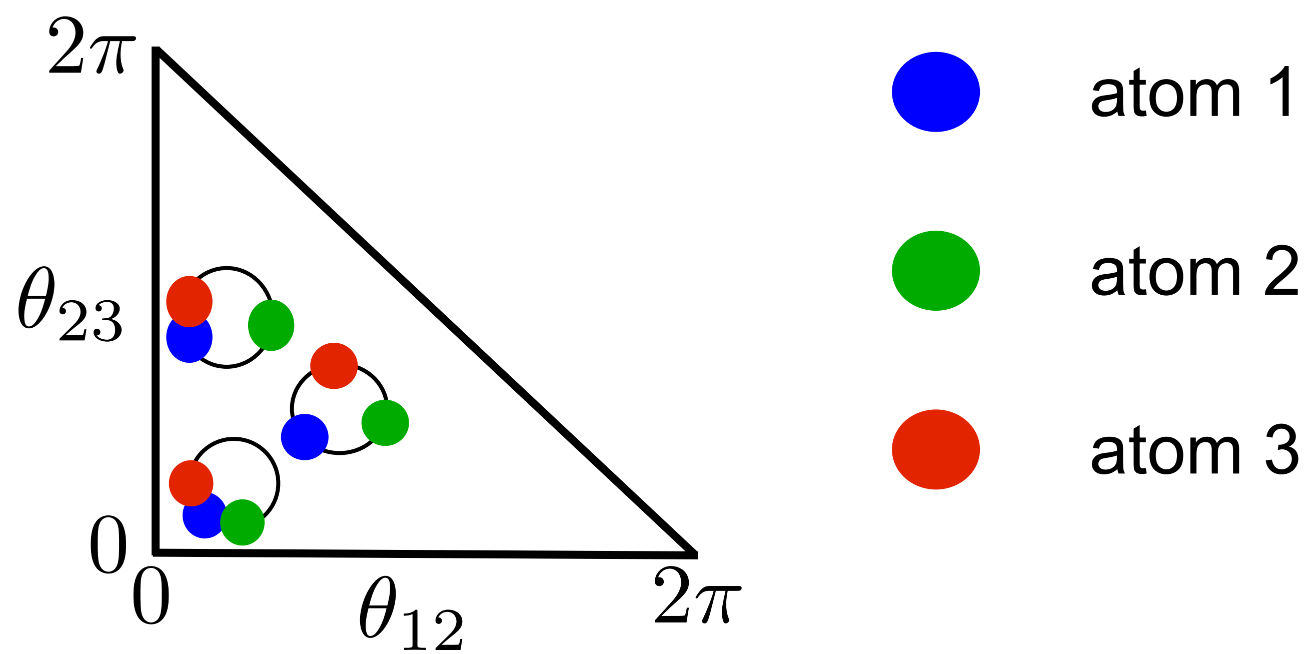

electronic dipole-dipole Hamiltonian:

$$H_{el} = -\mu^2 \begin{pmatrix} 0 & \frac{1}{R_{12}^3} & \frac{1}{R_{13}^3} \\ \frac{1}{R_{21}^3} & 0 & \frac{1}{R_{23}^3} \\ \frac{1}{R_{31}^3} & \frac{1}{R_{32}^3} & 0 \end{pmatrix}$$

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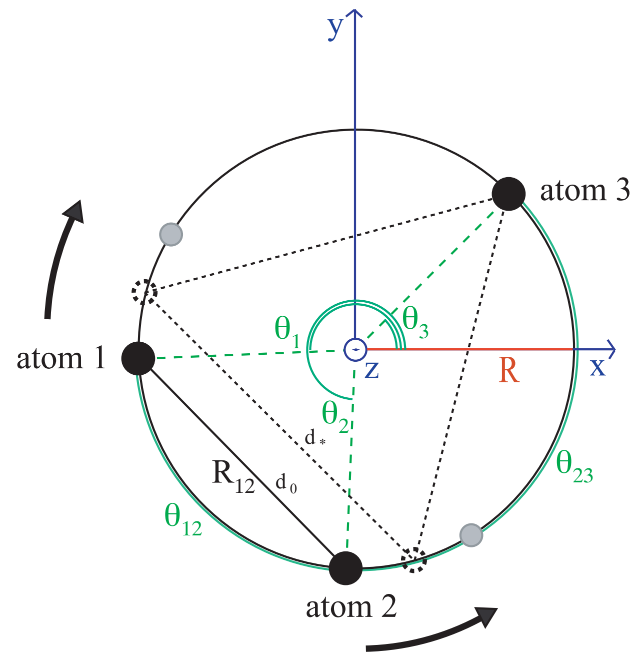
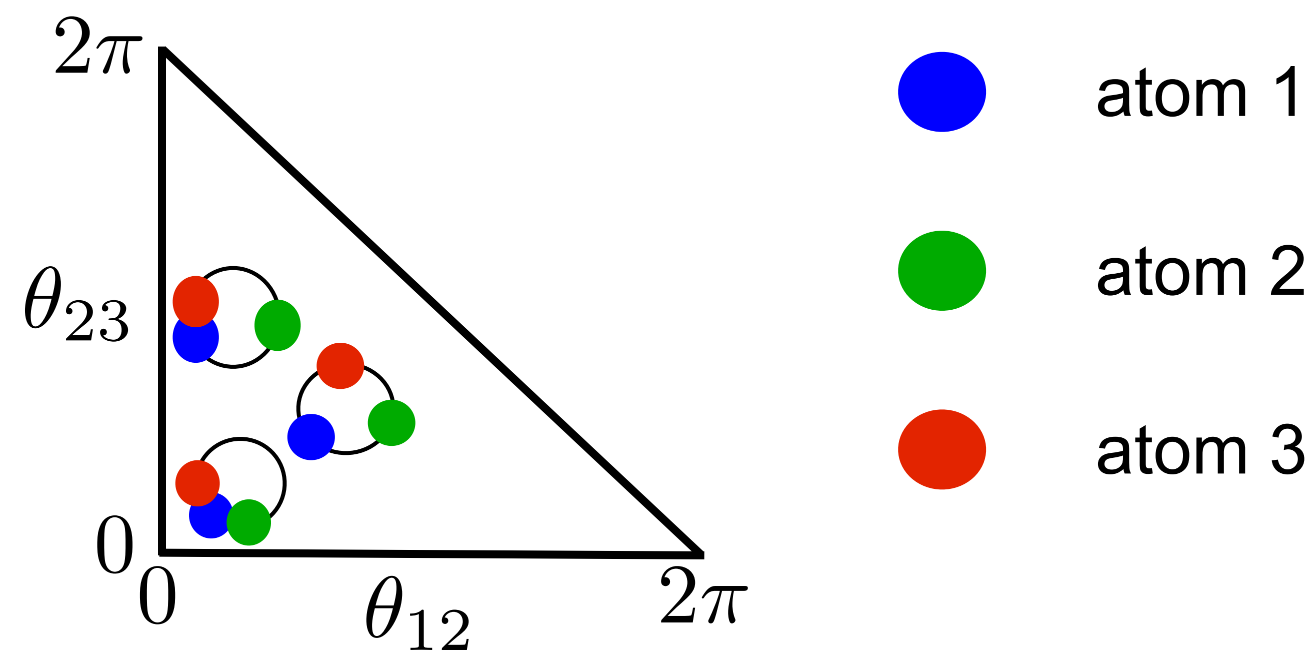


parameter space



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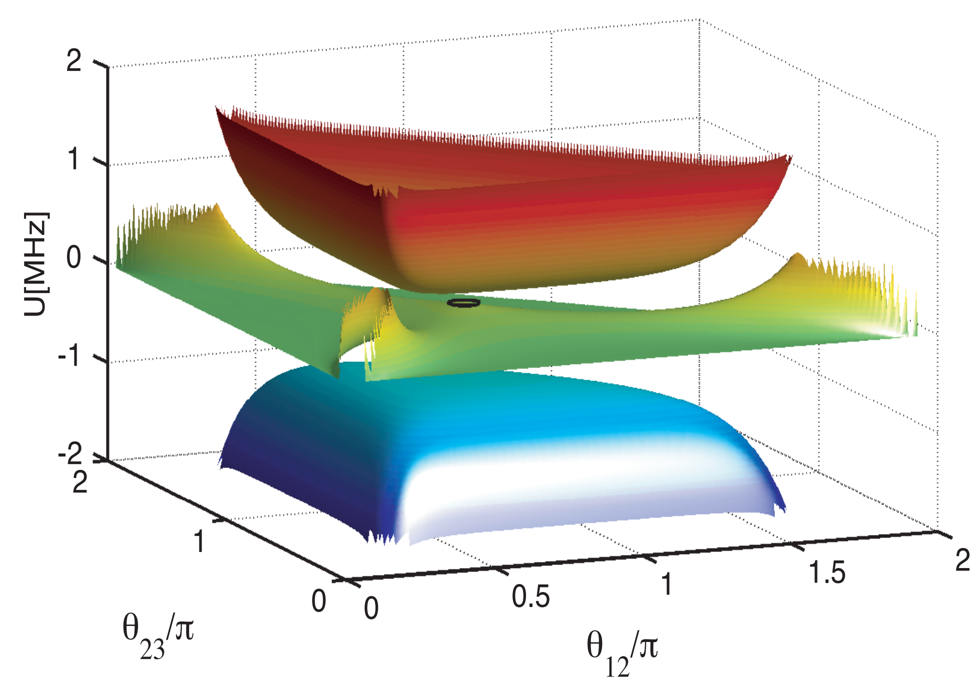
adiabatic potential surfaces



Ring trimer

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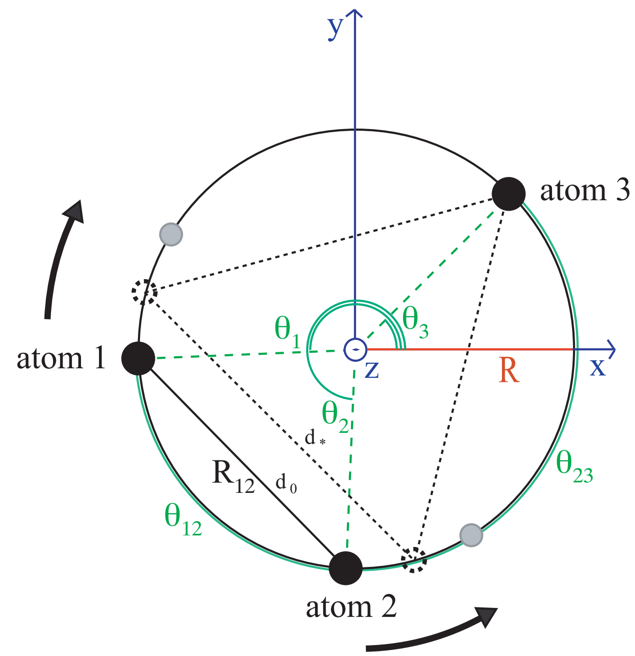
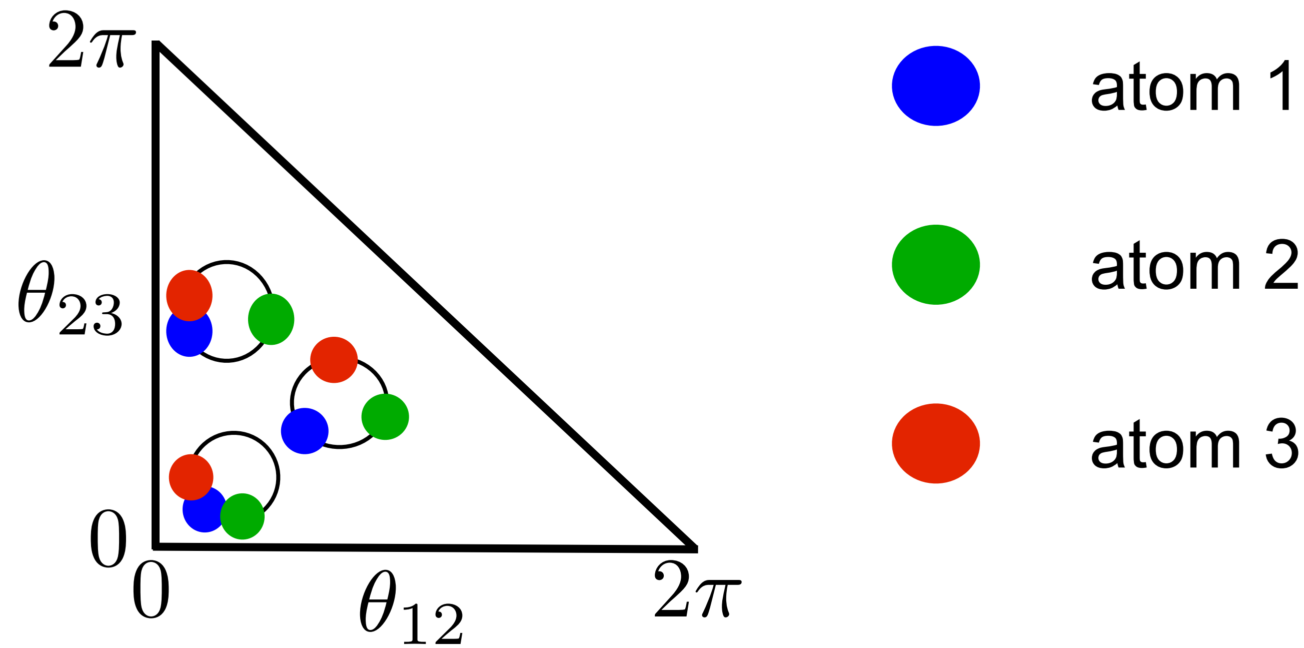


parameter space



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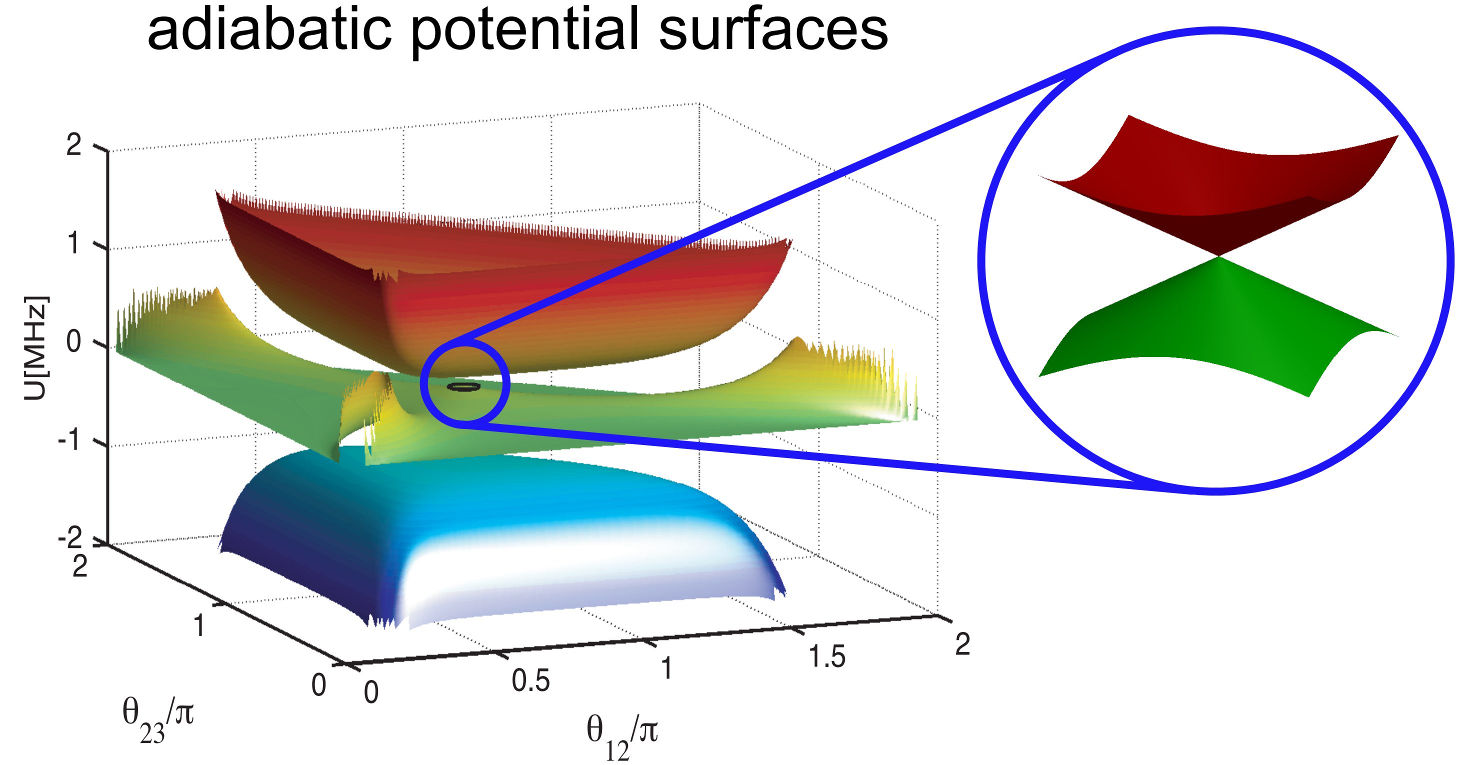
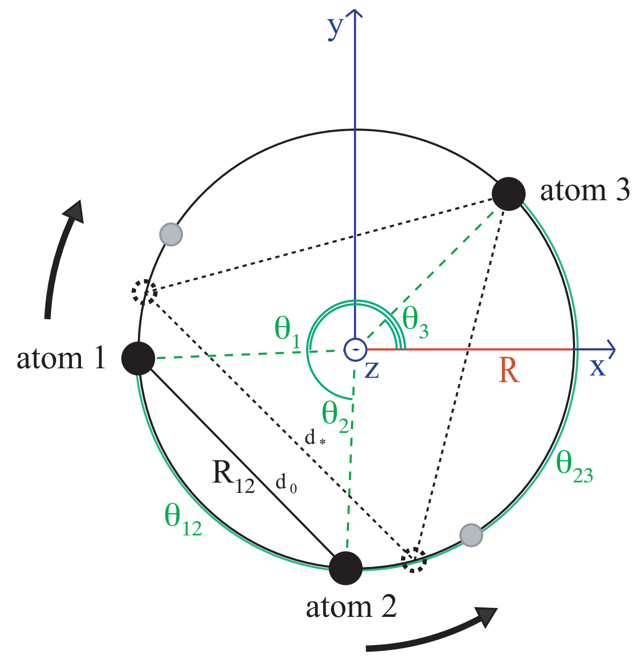


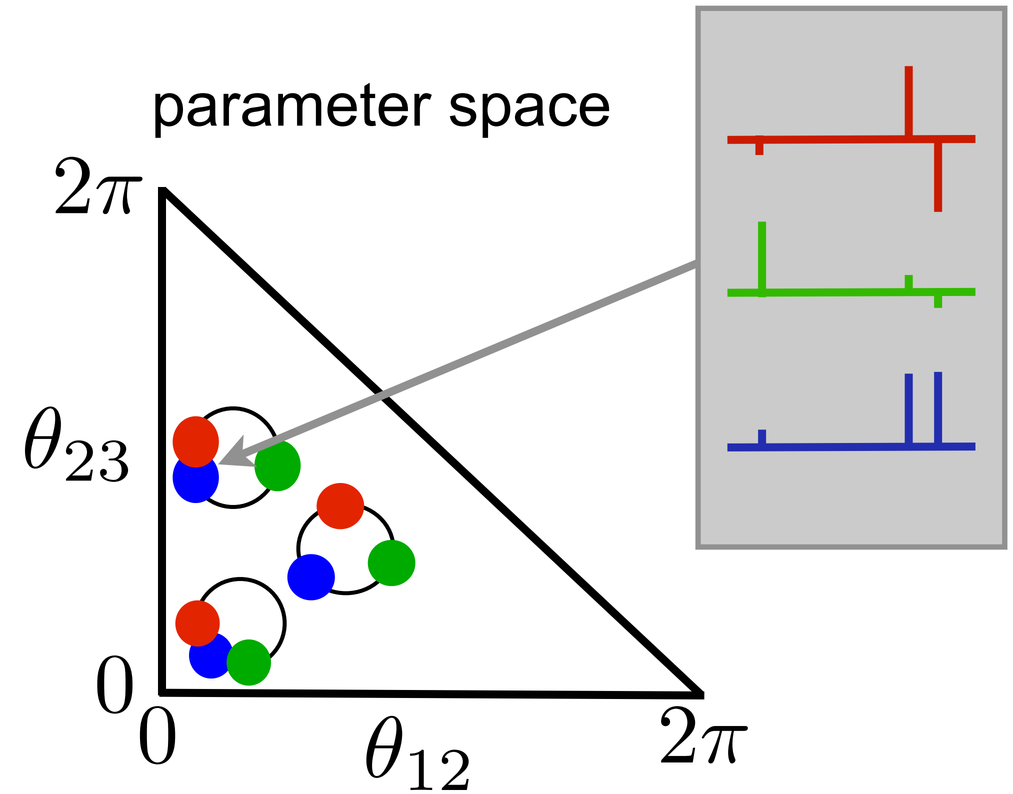
Ring trimer

exciton states

three atoms confined on ring



parameter space



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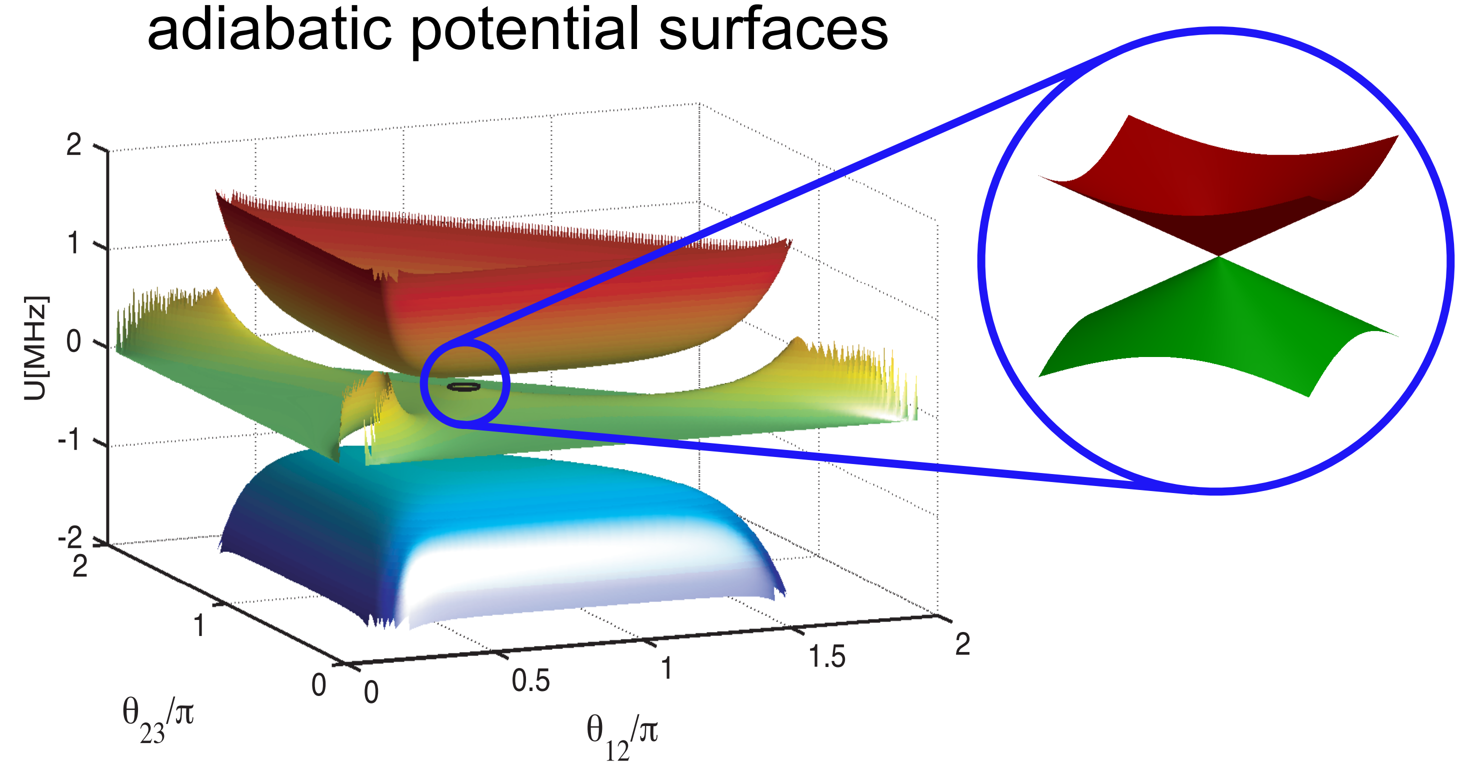
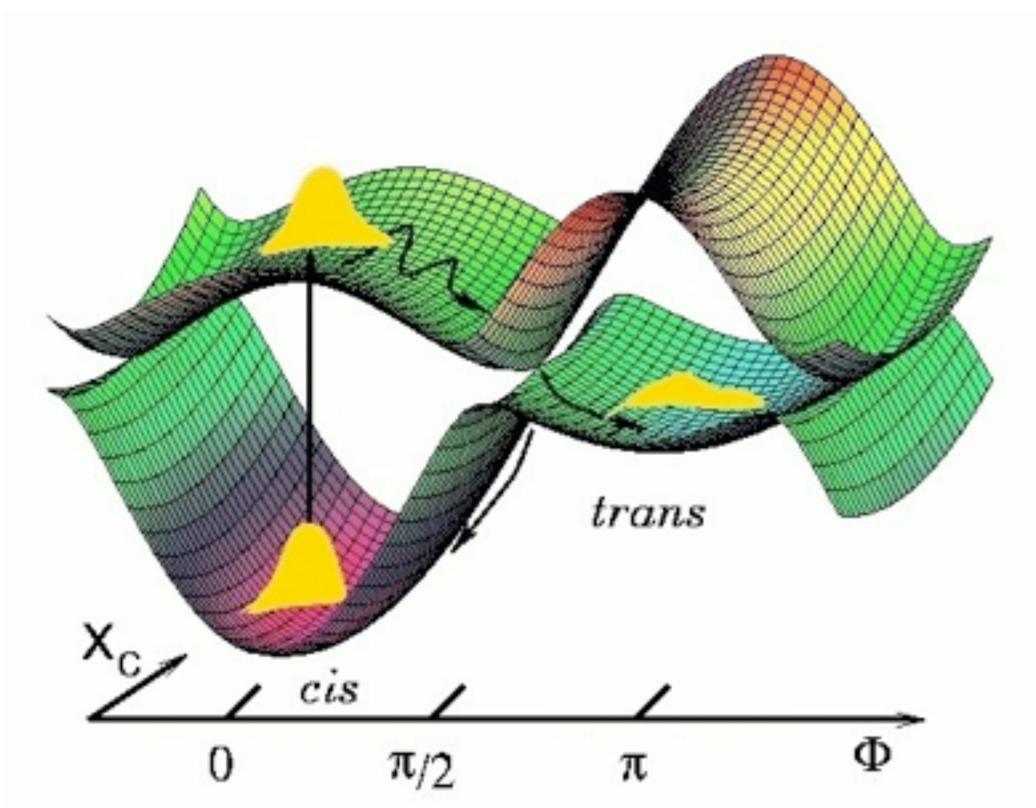


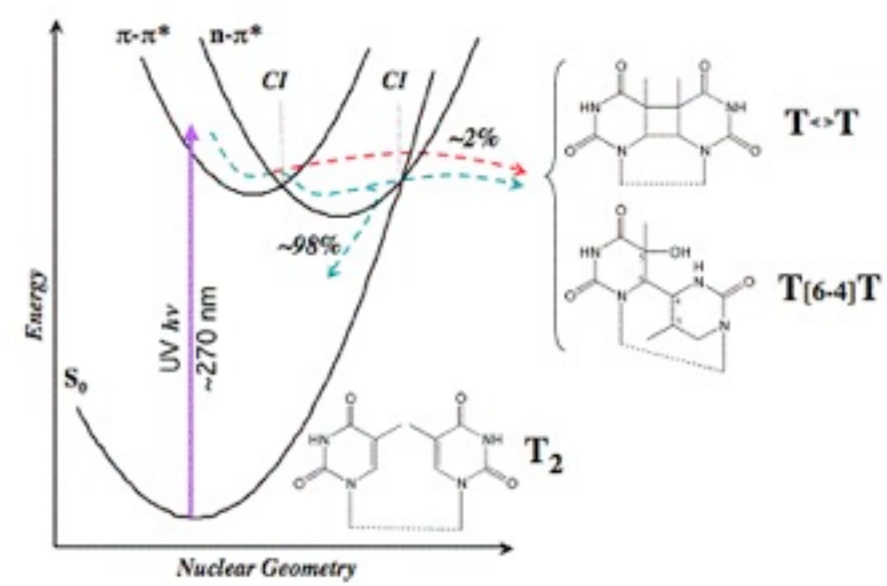
S. Wüster, A. Eisfeld, J.-M. Rost, Phys. Rev. Lett. ***106*** *153002 (2011).*

Conical intersections, Biochemistry/ Photochemistry

vision / photobiology



Thymine photo-chemistry



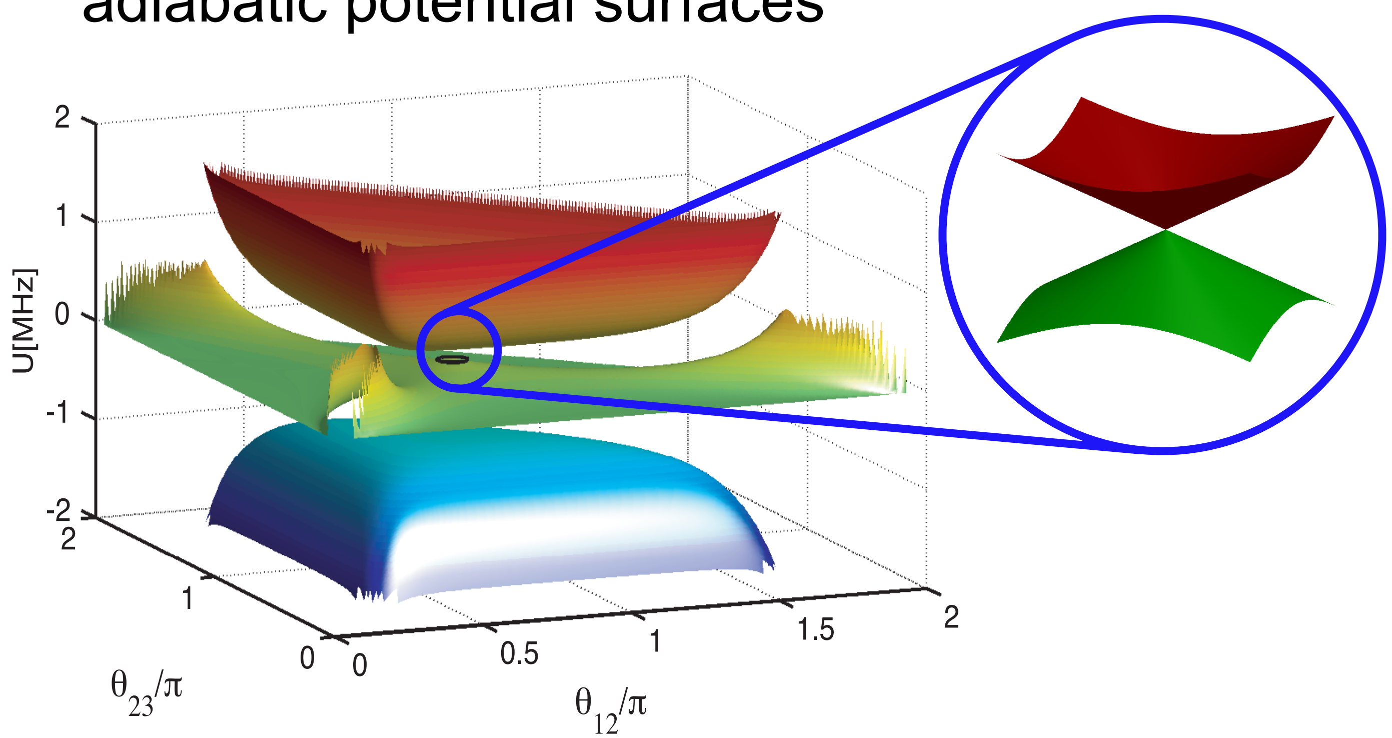
http://chem.chem.rochester.edu/~dmgrp/Research.html

S. Hahn and G. Stock
J. Phys. Chem. B **104** 1146 (2000).

also see e.g.:
S. Perun, A.L. Sobolewski and W. Domcke
J. Am. Chem. Soc. **127** 6257 (2005).

Conical intersections

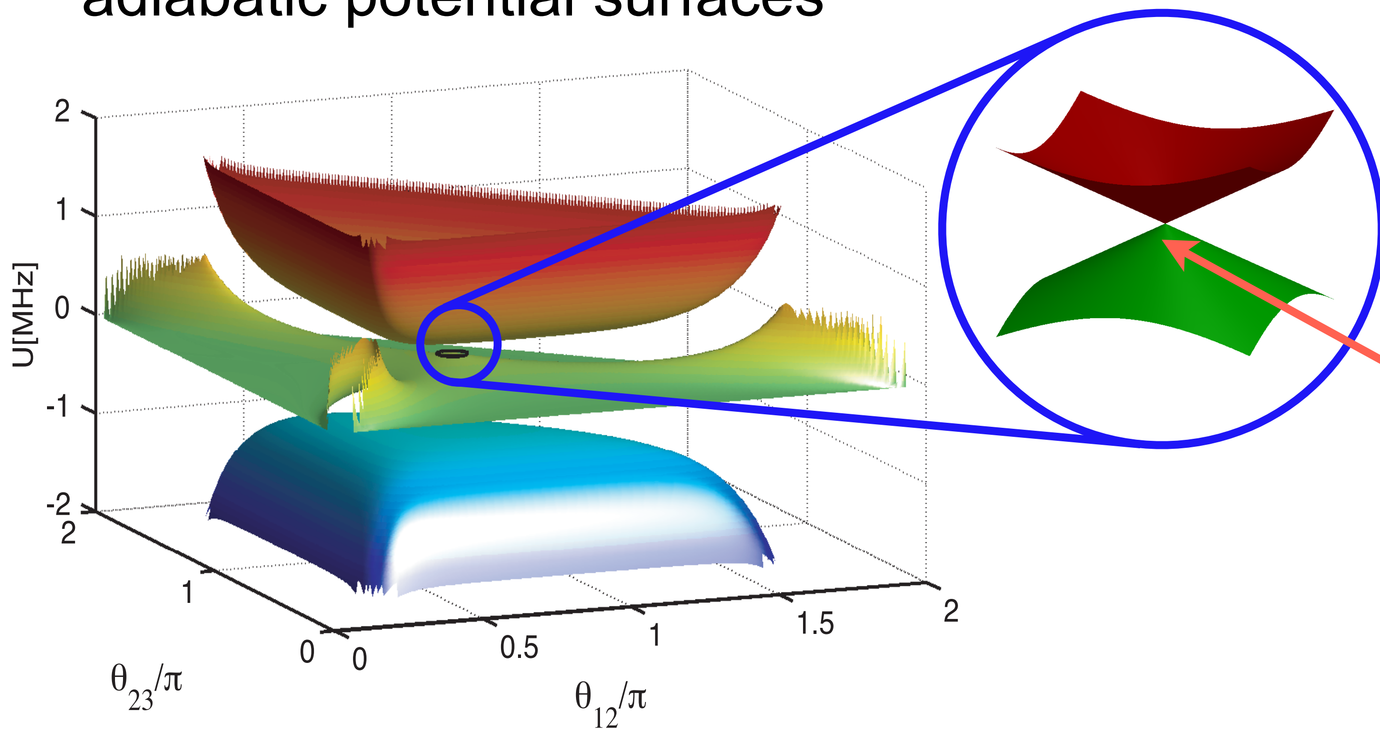
adiabatic potential surfaces



D.R. Yarkony
Rev. Mod. Phys **68** 985 (1996).

Conical intersections

adiabatic potential surfaces



D.R. Yarkony
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consequence I: non-adiabaticity

Conical intersections

adiabatic potential surfaces

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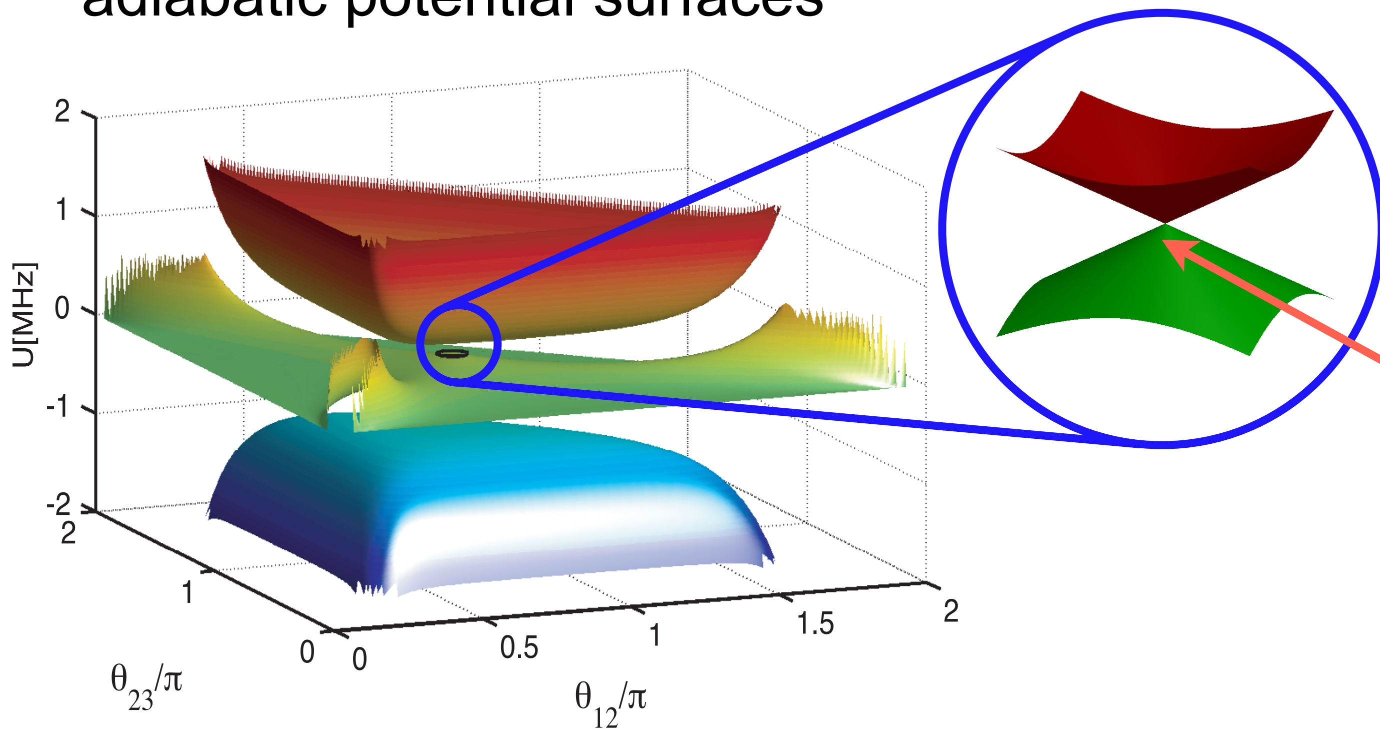
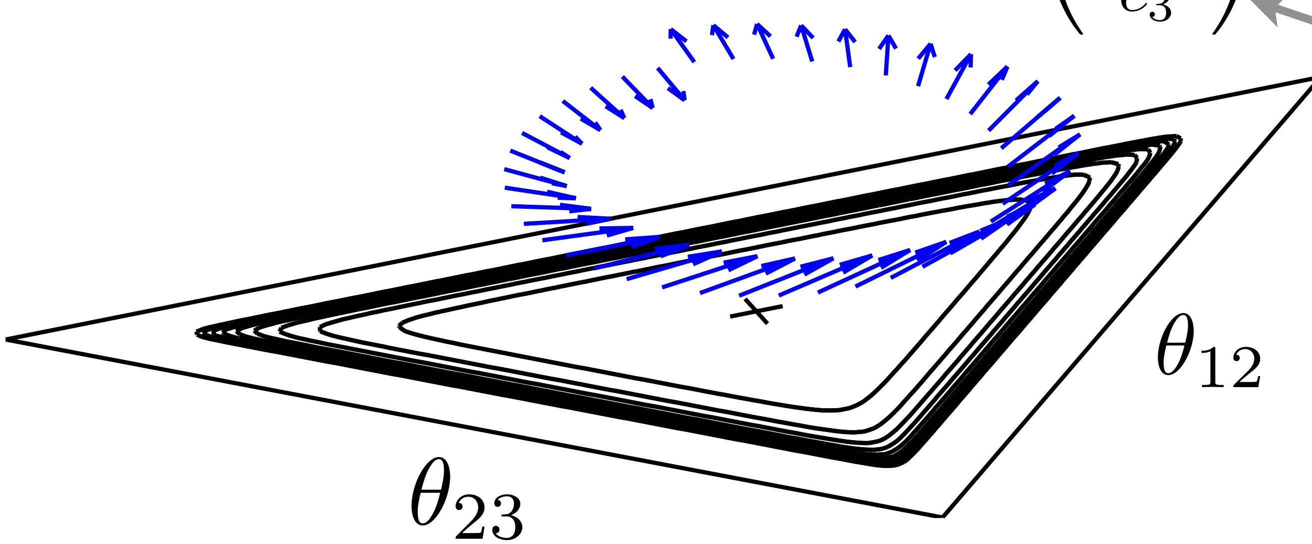
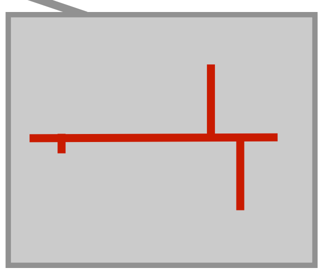


consequence I: non-adiabaticity

Repulsive exciton state

$$\vec{v}_{\rm rep} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$





Conical intersections

adiabatic potential surfaces

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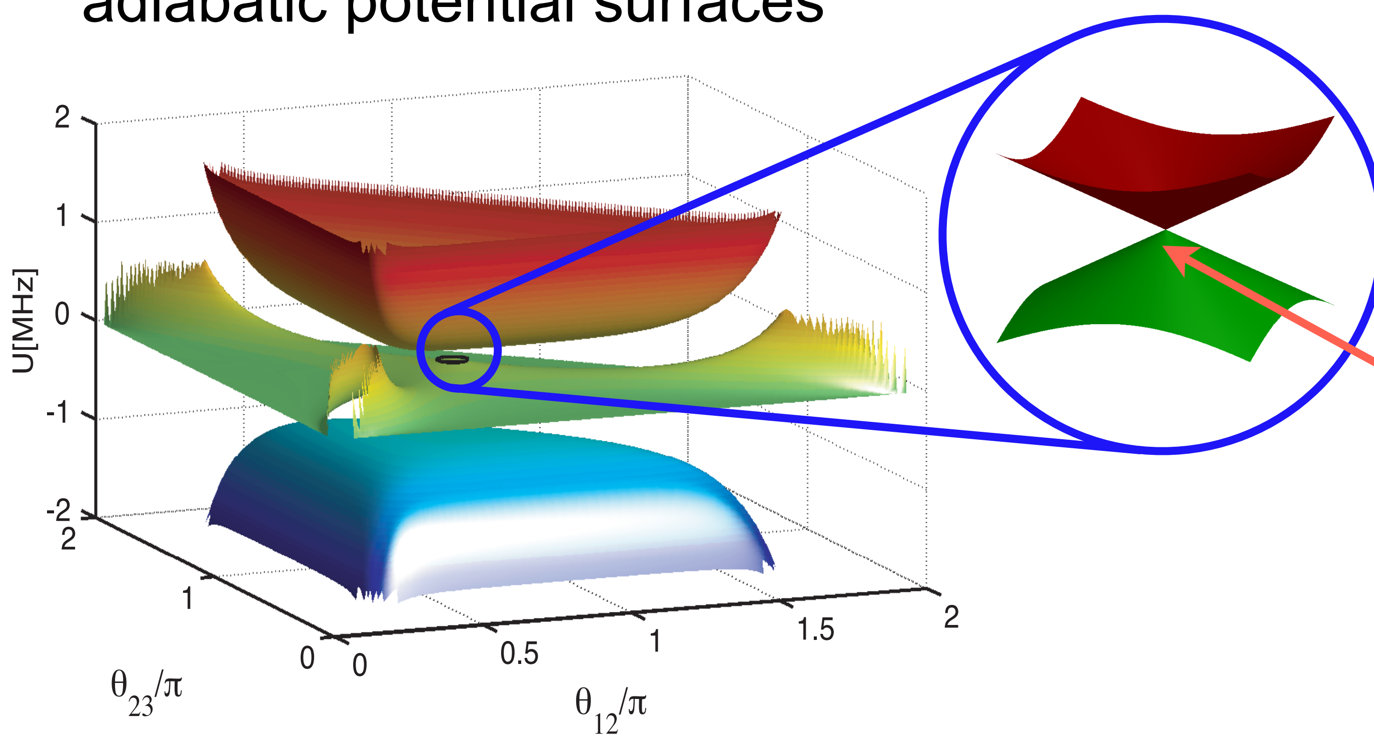

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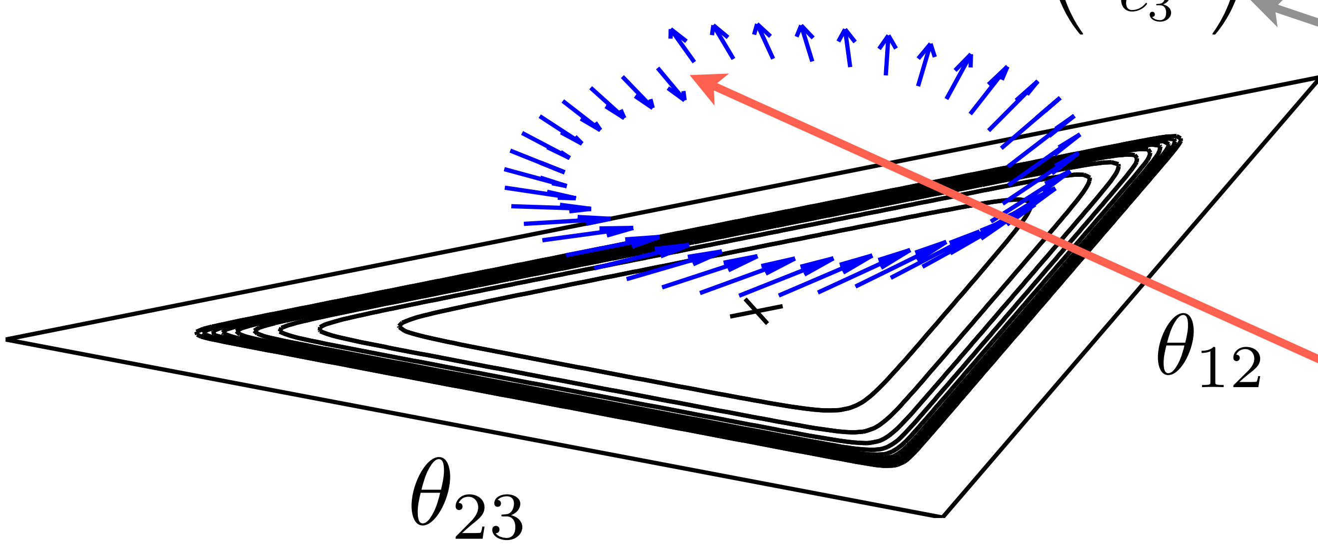

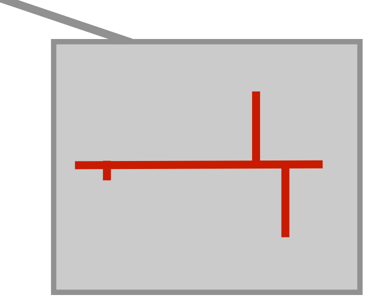

consequence II: geometric-phase

I: Conical intersections and the Born-Oppenheimer approximation

- Schrödinger's equation in Born-Oppenheimer *Separation*

$$i\hbar\frac{\partial}{\partial t}\phi_k(\mathbf{R}) = \left(\sum_n -\frac{\hbar^2}{2M}\nabla^2_{R_n} + U_k(\mathbf{R})\right)\phi_k(\mathbf{R}) + \sum_{m\neq k}\theta_{km}(\mathbf{R})\phi_m(\mathbf{R})$$

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- Non-adiabatic coupling terms:

$$\theta_{km}(\mathbf{R}) = \langle\varphi_k(\mathbf{R})| - \sum_n^N \frac{\nabla_{R_n}}{M}|\varphi_m(\mathbf{R})\rangle\nabla_{R_n}$$

$$+\frac{1}{2}\langle\varphi_k(\mathbf{R})| - \sum_n^N \frac{\nabla^2_{R_n}}{2M}|\varphi_m(\mathbf{R})\rangle$$

$$\Delta[\phi_n(\mathbf{R})|\,\varphi_n(\mathbf{R})\,\rangle]$$

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$$+\frac{1}{2}\langle\varphi_k(\mathbf{R})| - \sum_n^N \frac{\nabla^2_{R_n}}{2M}|\varphi_m(\mathbf{R})\rangle$$

- Hellmann-Feynman theorem: $\langle\,\varphi_k(\mathbf{R})\,|\nabla_{\mathbf{R}_n}|\,\varphi_m(\mathbf{R})\,\rangle = \dfrac{\langle\,\varphi_k(\mathbf{R})\,|\nabla_{\mathbf{R}_n}\hat{H}_{el}|\,\varphi_m(\mathbf{R})\,\rangle}{U_m(\mathbf{R}) - U_k(\mathbf{R})}$

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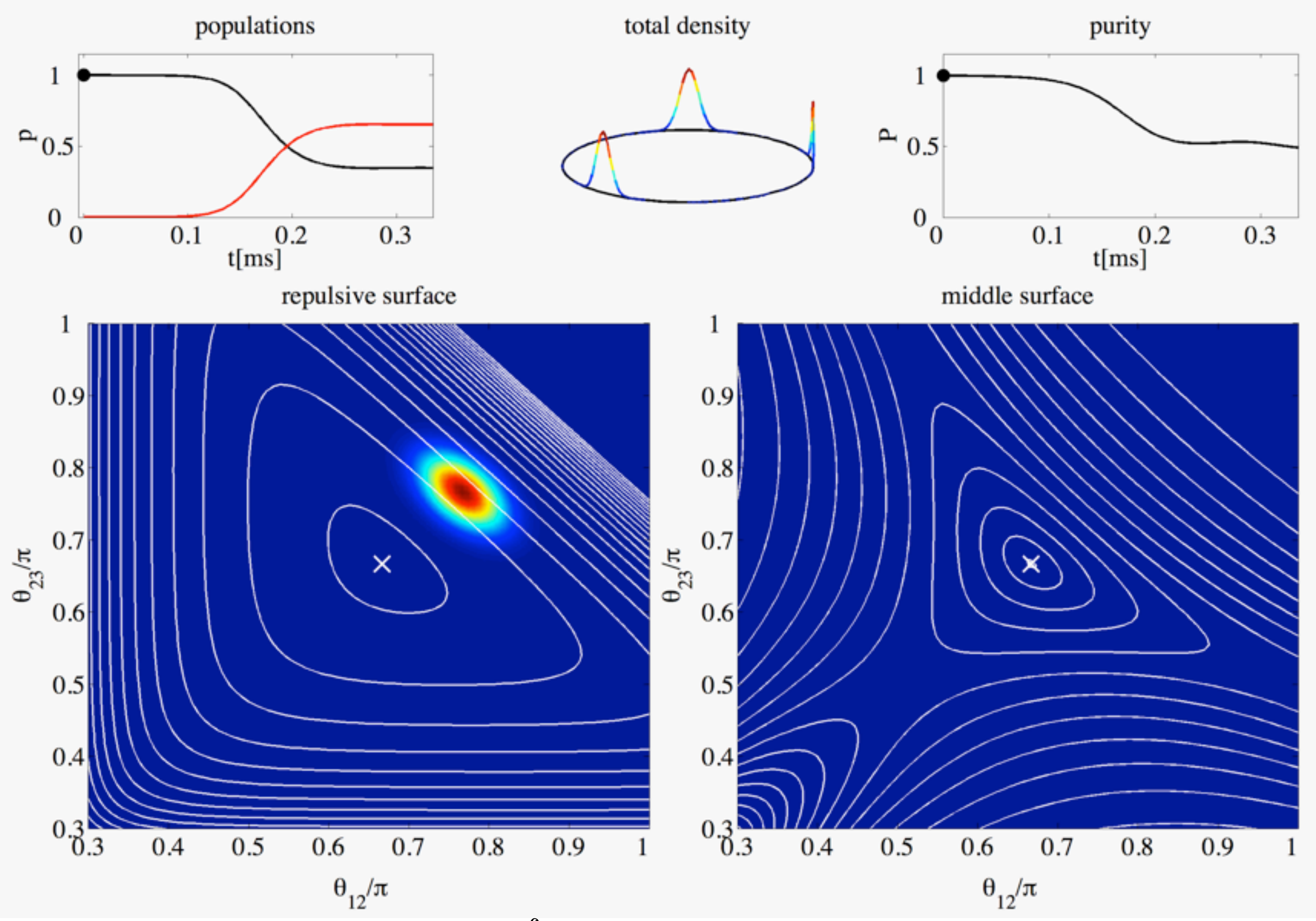
- At degenerate points (CI), non-adiabatic effect large for arbitrarily small velocity

Electronic decoherence

reduced electronic density matrix $\sigma_{nm} = \int d^N\mathbf{R}\ \phi_n^*(\mathbf{R})\phi_m(\mathbf{R})$

purity $P = \mathrm{Tr}[\hat{\sigma}^2]$

Electronic decoherence



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purity $P = \mathrm{Tr}[\hat{\sigma}^2]$

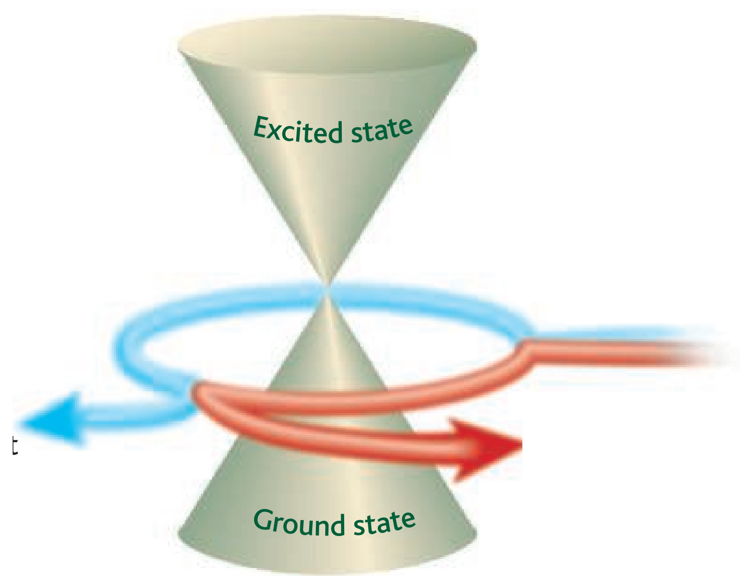
II: Conical intersections and the geometrical phase

- Derivative (non-adiabatic) coupling: $$f_{km} = \langle \varphi_k(\mathbf{R}) | - \sum_n^N \frac{\nabla_{R_n}}{M} | \varphi_m(\mathbf{R}) \rangle$$

- Can show around CI: $$\int_C \mathbf{f}_{km}(\tau) \cdot d\tau \rightarrow \pi$$

  D.R. Yarkony
  J. Phys. Chem. A **105** 6277 (2001).

- Adiabatic transport

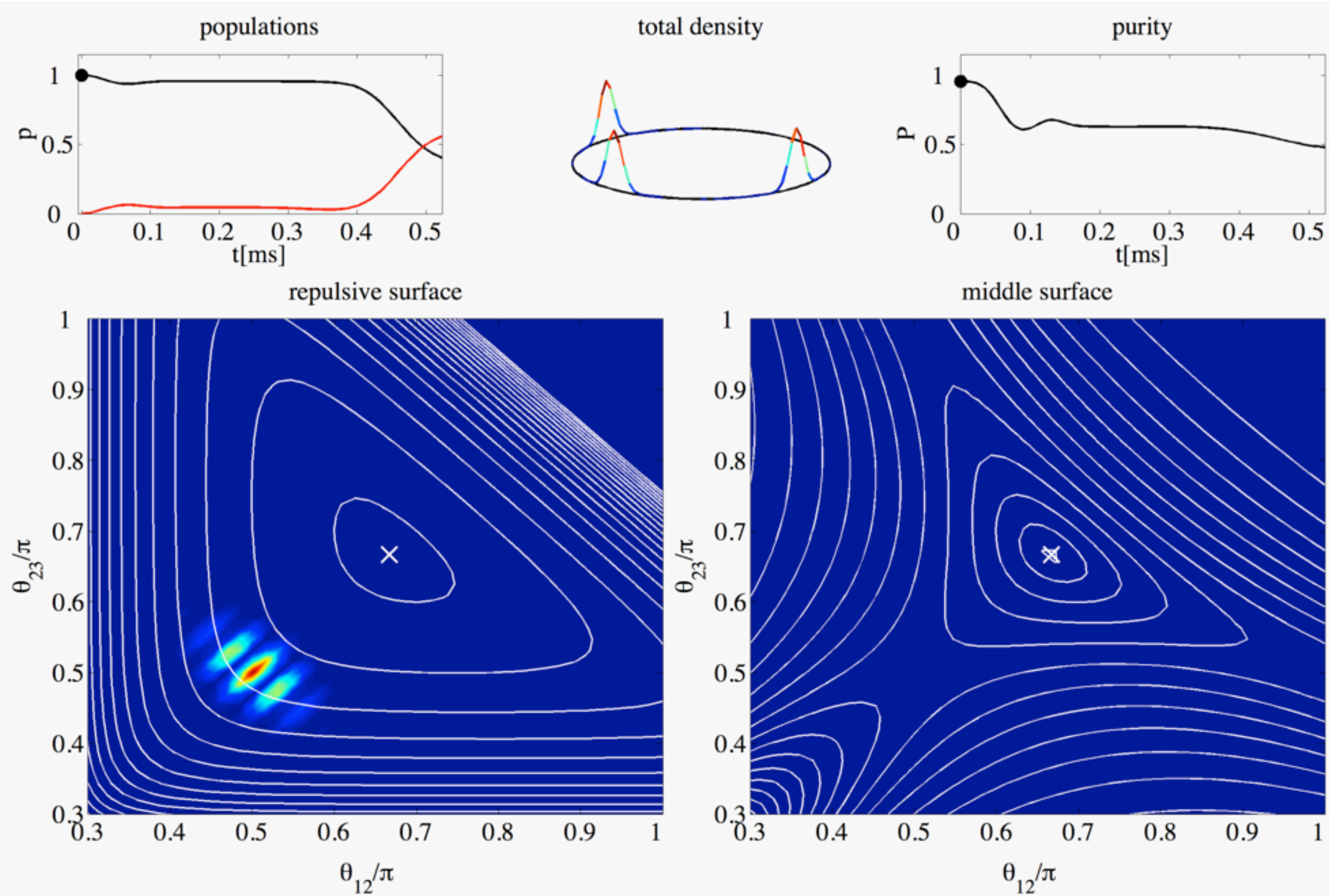


Dynamic versus geometric phase

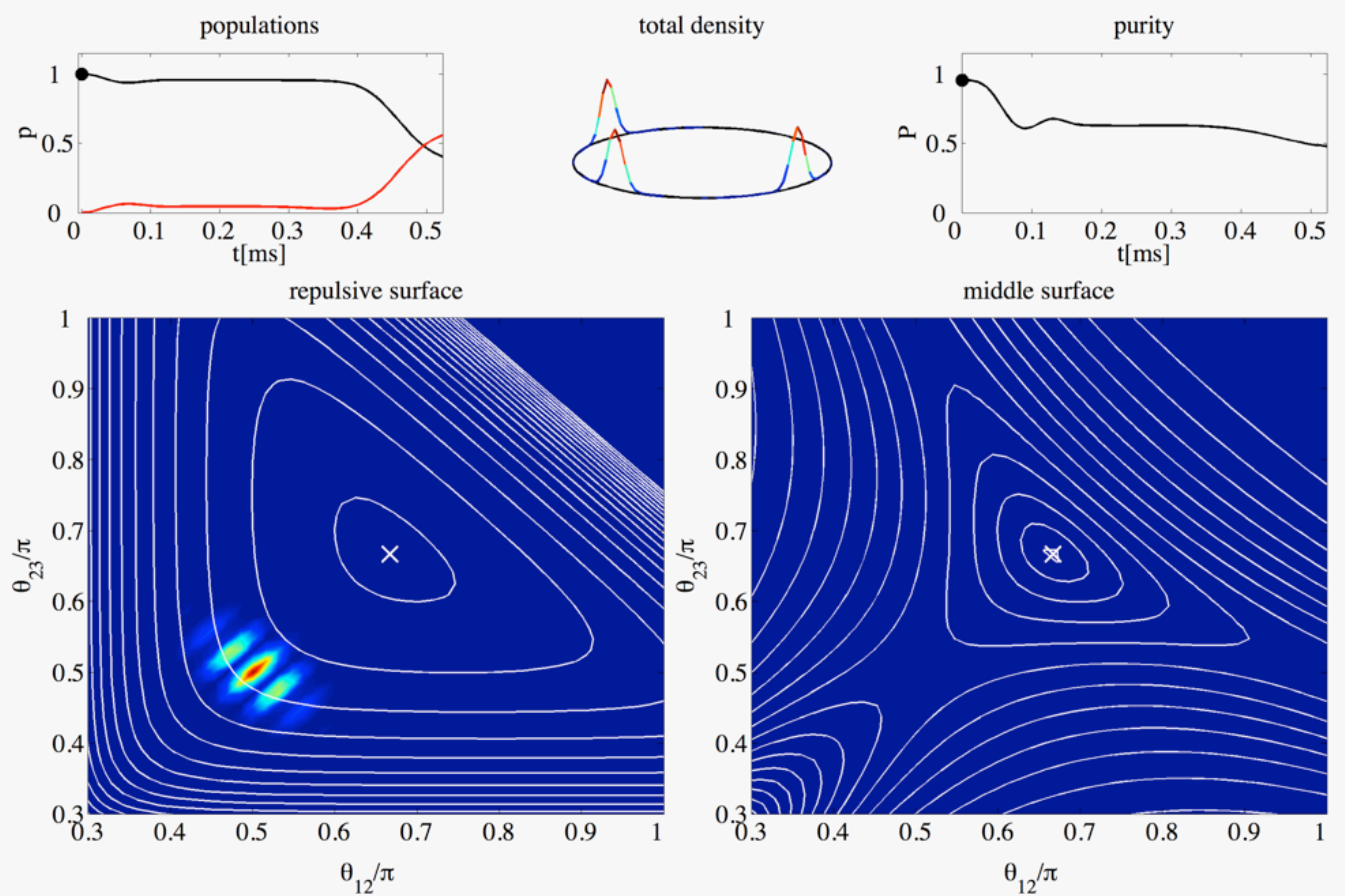
$$|\,\Psi(t)\,\rangle = |\,\varphi(\mathbf{R}(t))\,\rangle \exp\left[-i\int_0^t E(t')dt'/\hbar\right] \exp\left[i\gamma(\mathbf{R})\right]$$

Longuet-Higgins-Berry phase

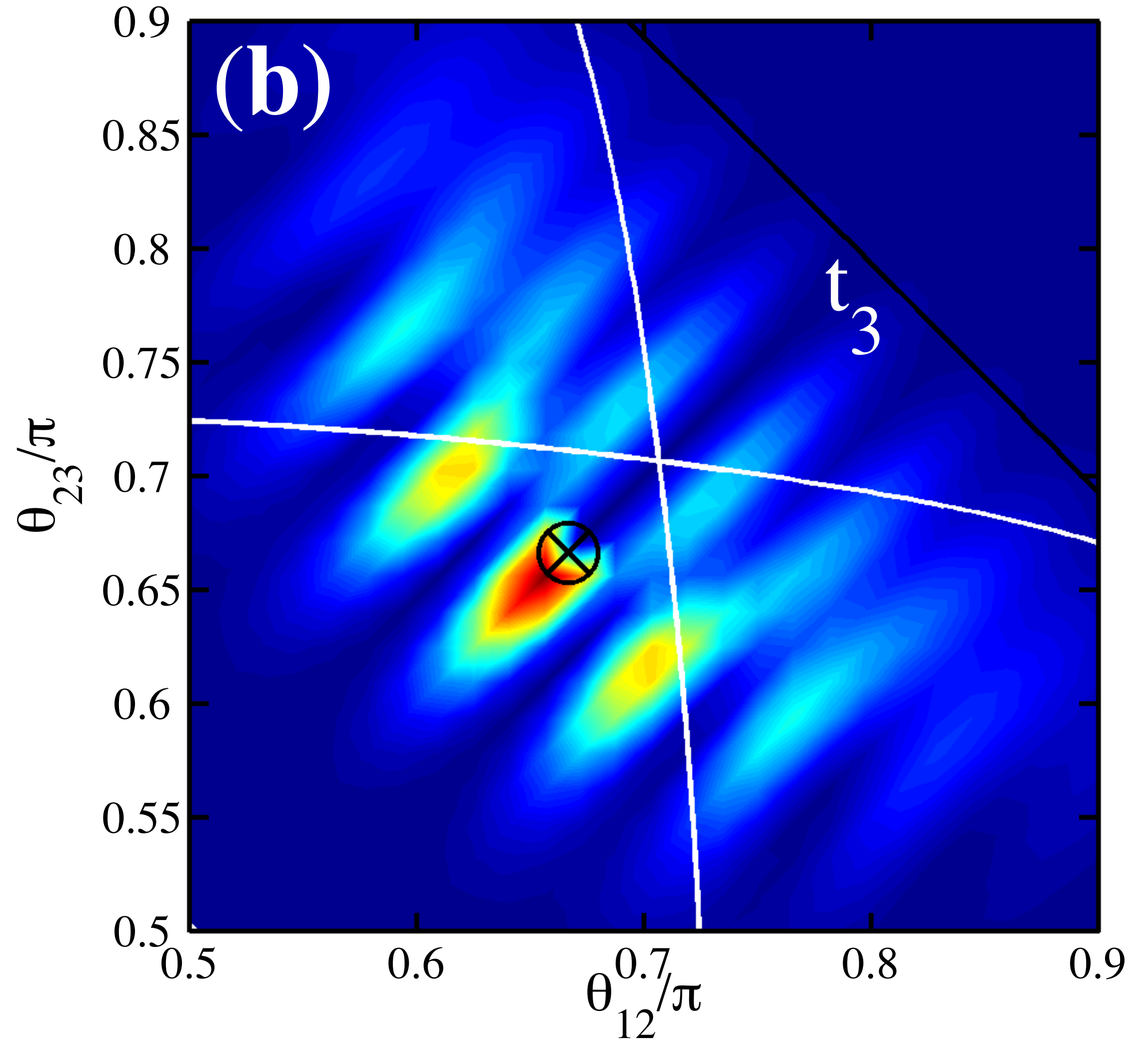
Longuet-Higgins-Berry phase

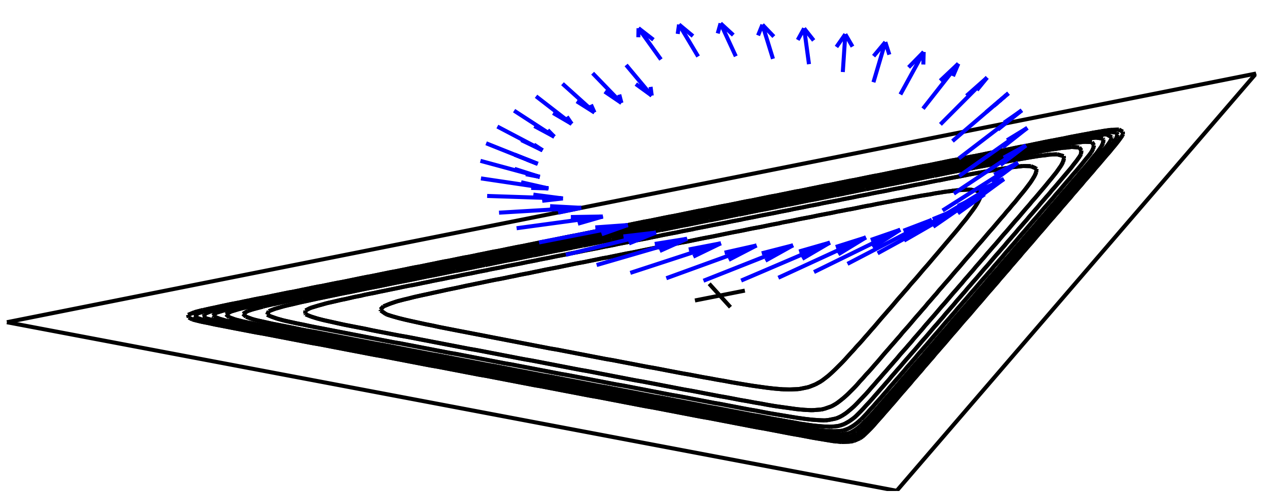


Longuet-Higgins-Berry phase



Longuet-Higgins-Berry phase



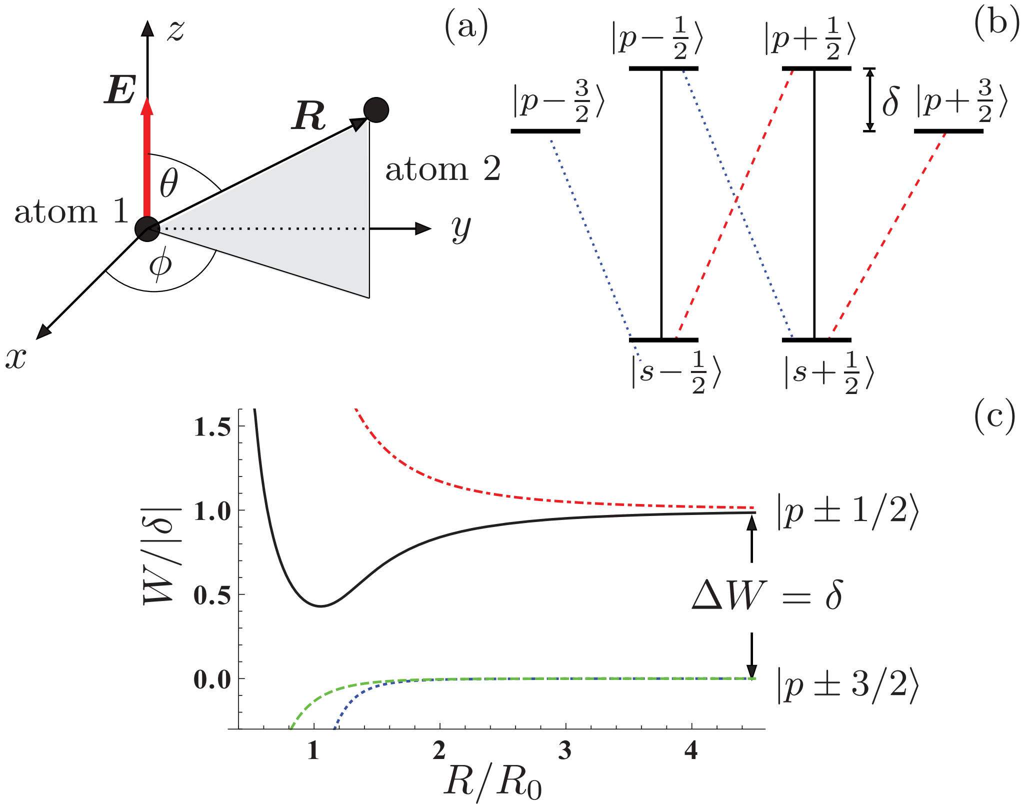


M.V. Berry,
Proc. Roy. Soc A **392** 45 (1984).

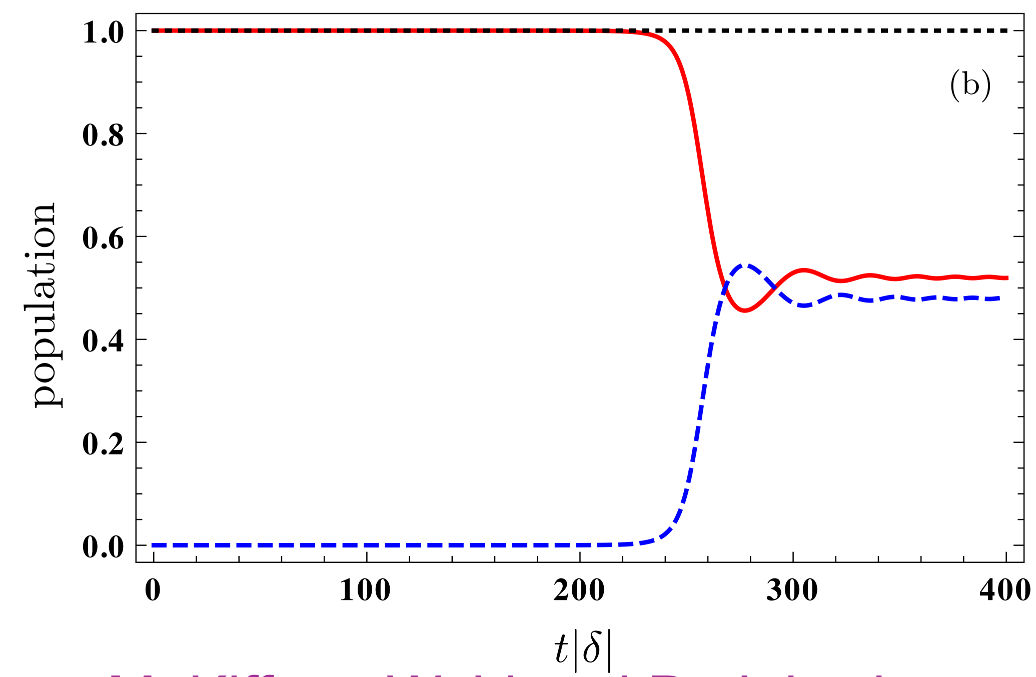
H.C. Longuet-Higgins,
Proc. Roy. Soc A **344** 147 (1975).

CIs in dipole-dipole bound molecules

- Dimer with more complicated state space and external fields:

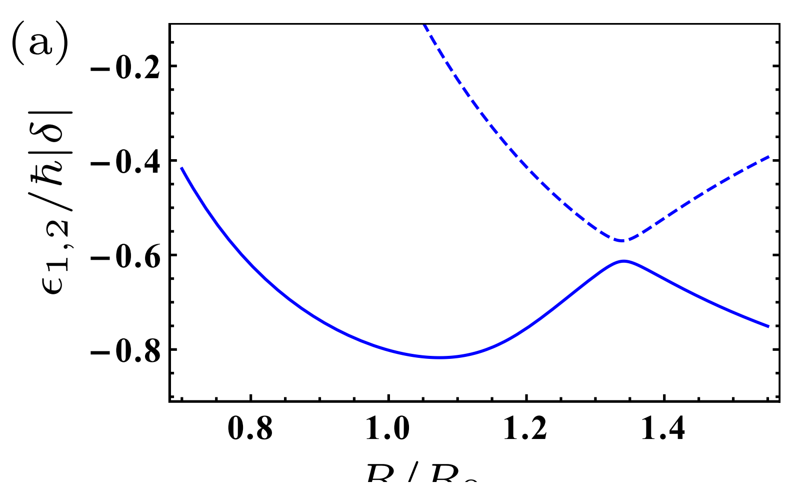


- Conical intersection crossing



M. Kiffner, W. Li and D. Jaksch, J. Phys. B **46** 134008 (2013).

- Selected molecular potential exhibit conical intersection



M. Kiffner, H. Park, W. Li and T.F. Gallagher Phys. Rev. A **86** 031401(R) (2012).

M. Kiffner, W. Li and D. Jaksch, Phys. Rev. Lett. **110** 170402 (2013).

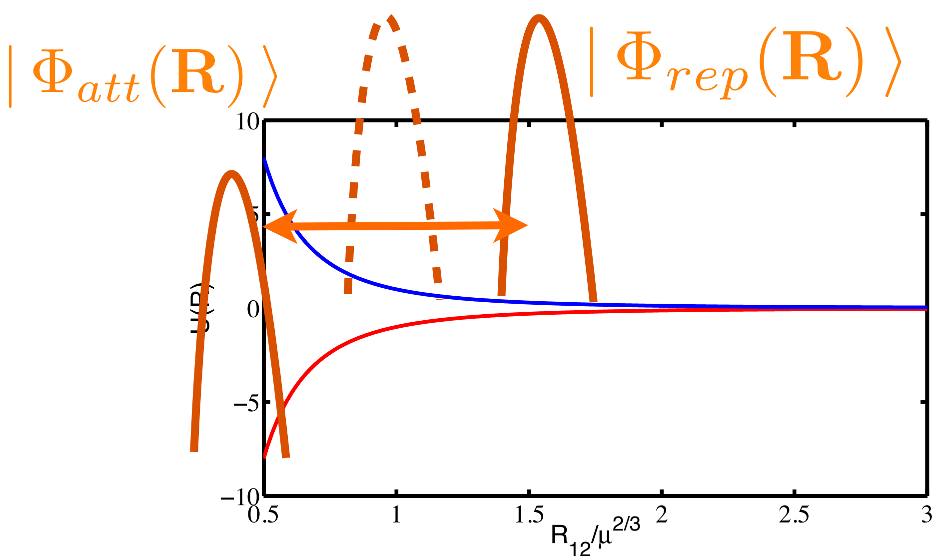
(7) Summary

- Dipole-dipole: links motion and state

excitation transport

unfrozen Rydberg gases

multi Born-Oppenheimer surfaces



- Methods:

Schrödinger's equation

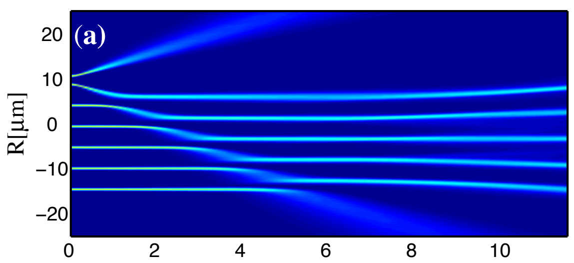
Tully's surface hopping

Ehrenfest method

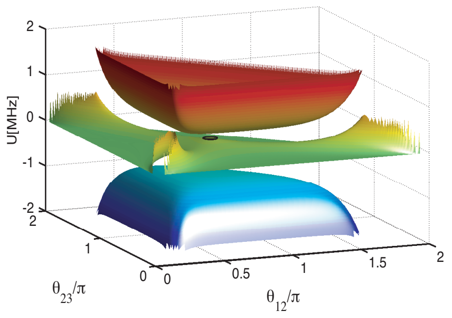
$$M\ddot{\mathbf{R}}(t) = -\nabla_R U_k(\mathbf{R})$$

- Applications:

Entanglement transport



Visualize dynamics at conical intersections (chemistry)



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Thanks for your attention