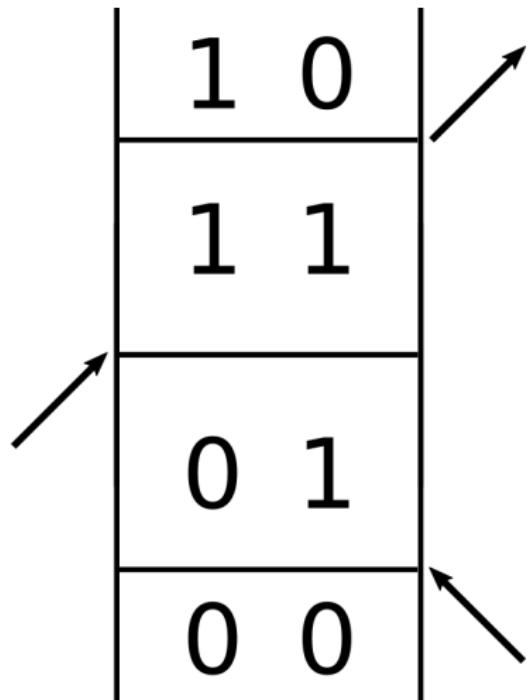


Molecular Excitons

Mike Reppert

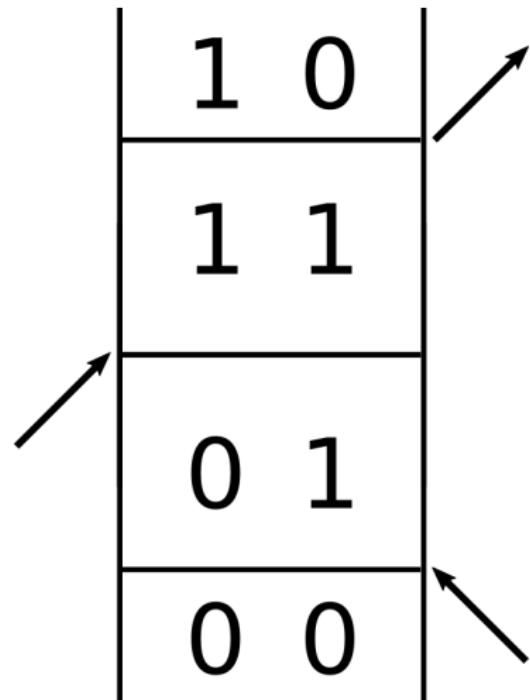
November 4, 2019

We developed a **diagrammatic expansion** for non-linear spectroscopic response functions.



We developed a **diagrammatic expansion** for nonlinear spectroscopic response functions.

Today: Molecular exciton models for nonlinear spectroscopy



Some Historical Perspective

JANUARY 1, 1931

PHYSICAL REVIEW

VOLUME 37

ON THE TRANSFORMATION OF LIGHT INTO HEAT IN SOLIDS. I¹

By J. FRENKEL

DEPARTMENT OF PHYSICS, UNIVERSITY OF MINNESOTA

(Received November 25, 1930)

ABSTRACT

Starting from the analogy between a crystal and molecule, it is shown that the electronic excitation, forming the first step in the process of light absorption, is not confined to a particular atom, but is diluted between all of them in the form of "excitation waves," similar to sound waves which are used to describe the heat motion in the same crystal. Owing to the interaction between the atoms the excitation state is split up into substates whose number is equal to the number of atoms n (excitation multiplet). By superposing several excitation waves "excitation packets" can be constructed representing the travelling of the excitation state from one atom to another. To each excitation sub-state there corresponds a definite crystal structure (lattice constant, vibration frequencies) slightly different from that of the normal, and giving rise to slightly different vibrational states. This influence of the excitation on the vibrational states provides an indirect coupling between them, which allows the excitation energy to be shared between a few hundred heat-oscillators with practically no direct coupling nor anharmonicity in a radiationless transition which forms the second state of the process of light absorption.

Some Historical Perspective

DECEMBER, 1938

JOURNAL OF CHEMICAL PHYSICS

VOLUME 6

Migration and Photochemical Action of Excitation Energy in Crystals

JAMES FRANCK, *University of Chicago, Chicago, Illinois*

AND

EDWARD TELLER, *George Washington University, Washington, D. C.*

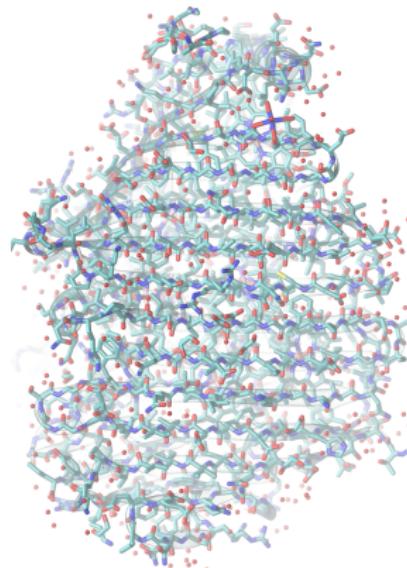
(Received October 1, 1938)

A crystal which has absorbed a light quantum can be treated either as an assembly of molecules or else as a giant molecule. If the exchange of excitation energy between crystal cells is slow as compared to the periods of vibration, the first description is preferable; if it is fast, the second picture is better. Both cases are discussed in connection with the following question: To what extent can excitation energy absorbed by an arbitrary cell of the crystal be used photochemically at a specific point which may be far removed from the absorbing cell? The results are applied to the behavior of polymerized pseudoisocyanines, to the hypothetical photosynthetic unit and to the theory of sensitized photographic plates.

Molecular Excitons

A **molecular exciton** is a delocalized excited state created by interactions between nearby molecules

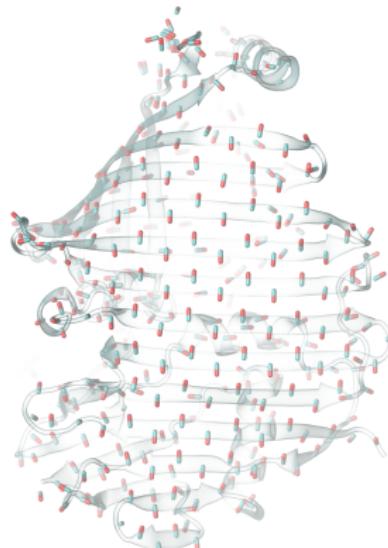
NB: The molecular exciton picture is an **approximation** to reality that drastically simplifies many problems.



Molecular Excitons

A **molecular exciton** is a delocalized excited state created by interactions between nearby molecules

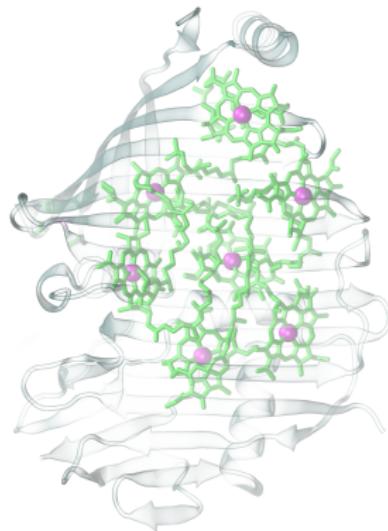
NB: The molecular exciton picture is an **approximation** to reality that drastically simplifies many problems.



Molecular Excitons

A **molecular exciton** is a delocalized excited state created by interactions between nearby molecules

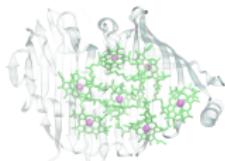
NB: The molecular exciton picture is an **approximation** to reality that drastically simplifies many problems.



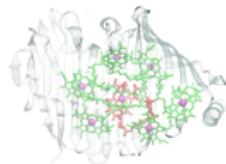
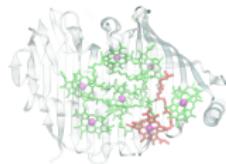
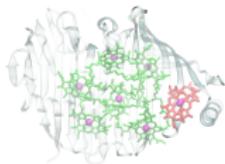
The Site Basis

The **site basis** is an orthonormal basis consisting of local-excitation wavefunctions

Ground State:

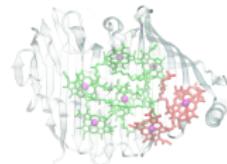
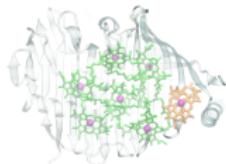


Singly-Excited States:



...

Multiply-Excited States:



...

The Site Basis

The **site basis** is an orthonormal basis consisting of local-excitation wavefunctions:

Ground State:

$$\Phi_0 = \phi_0(x_1)\phi_0(x_2)\dots\phi_0(x_n)$$

Singly-Excited States:

$$\Phi_1 = \phi_1(x_1)\phi_0(x_2)\dots\phi_0(x_n)$$

⋮

$$\Phi_n = \phi_0(x_1)\phi_0(x_3)\dots\phi_0(x_{n-1})\phi_1(x_n)$$

Multiply-Excited States:

$$\Phi_{11} = \phi_2(x_1)\phi_0(x_2)\dots\phi_0(x_n)$$

$$\Phi_{12} = \phi_1(x_1)\phi_1(x_2)\phi_0(x_3)\dots\phi_0(x_n)$$

⋮

The Site Basis

The **site basis** is an orthonormal basis consisting of local-excitation wavefunctions

Ground State:

$$|0\rangle = |0, \dots, 0\rangle$$

Singly-Excited States:

$$|1\rangle = |\underset{\vdots}{\textcolor{red}{1}}, 0, \dots, 0\rangle$$

$$|n\rangle = |0, \dots, 0, \underset{\vdots}{\textcolor{red}{1}}\rangle$$

Multiply-Excited States:

$$|11\rangle = |\underset{\vdots}{\textcolor{red}{2}}, 0, \dots, 0\rangle$$

$$|12\rangle = |\underset{\vdots}{\textcolor{red}{1}}, \underset{\vdots}{\textcolor{red}{1}}, 0, \dots, 0\rangle$$

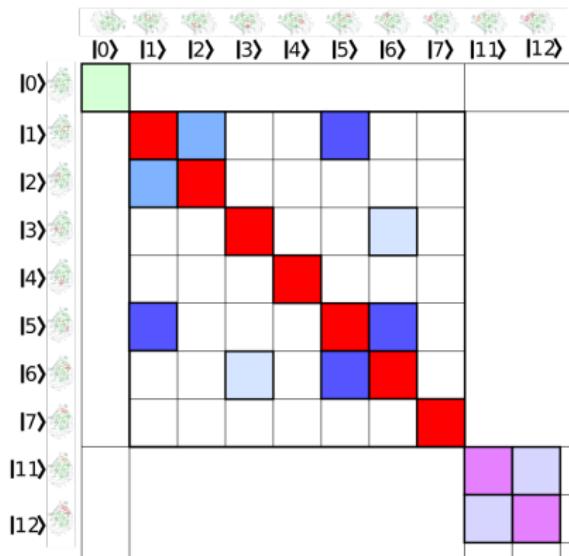
The Site-Basis Hamiltonian

The **Hamiltonian matrix** for a molecular exciton system is obtained by taking matrix elements in a particular subspace, e.g., singly-excited states:

	$ 1\rangle$	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$	$ 5\rangle$	$ 6\rangle$	$ 7\rangle$
$ 1\rangle$	Red	Light Blue			Dark Blue		
$ 2\rangle$	Light Blue	Red					
$ 3\rangle$			Red			Light Blue	
$ 4\rangle$				Red			
$ 5\rangle$	Dark Blue				Red	Dark Blue	
$ 6\rangle$			Light Blue		Dark Blue	Red	
$ 7\rangle$							Red

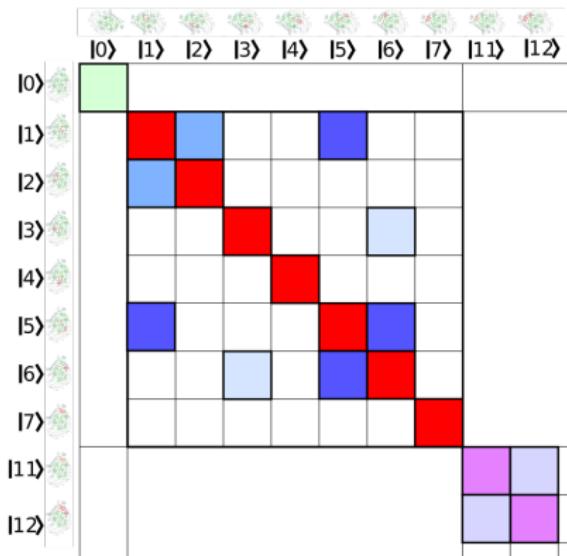
Intra-Manifold Coupling

Hold up! What about inter-subspace interactions?



Intra-Manifold Coupling

Hold up! What about inter-subspace interactions?



Answer: The **large energy differences** between excitation manifolds effectively weakens coupling!

The Exciton Basis

Molecular eigenstates can be calculated by **diagonalizing** the Hamiltonian matrix:

$$\hat{U}^\dagger \hat{H} \hat{U} = \hat{D}$$

	1>	2>	3>	4>	5>	6>	7>
1>	Dark Blue						
2>	Light Blue						
3>			Dark Blue				
4>	Light Blue			Dark Blue			
5>					Dark Blue		
6>		Dark Blue				Dark Blue	
7>				Dark Blue			Dark Blue

	1>	2>	3>	4>	5>	6>	7>
1>	Dark Red	Light Blue					
2>	Light Blue	Red					
3>		Red				Light Blue	
4>			Dark Red				
5>	Blue			Red	Blue		
6>				Blue			
7>					Red		Light Red

	1>	2>	3>	4>	5>	6>	7>
1>	Dark Blue	Light Blue					
2>	Dark Blue						
3>							
4>			Dark Blue				
5>				Dark Blue	Light Blue		
6>				Dark Blue		Dark Blue	
7>					Dark Blue		Dark Blue

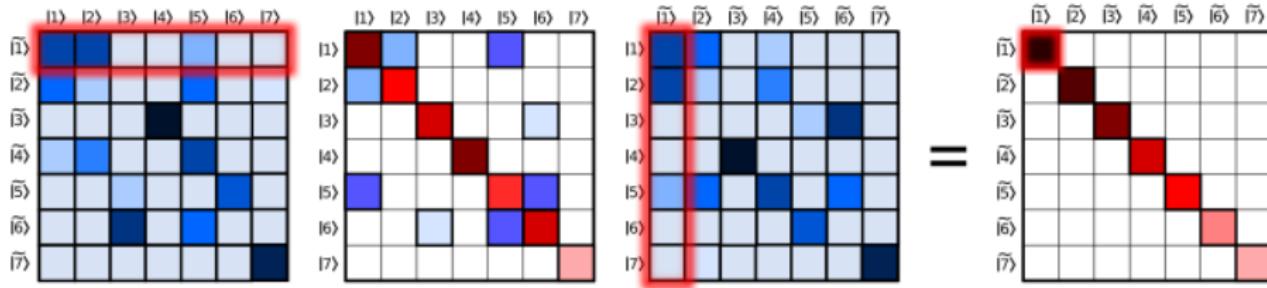
=

	1>	2>	3>	4>	5>	6>	7>
1>	Dark Red						
2>			Dark Red				
3>							
4>				Dark Red			
5>						Red	
6>							Red
7>							Red

The Exciton Basis

Molecular eigenstates can be calculated by **diagonalizing** the Hamiltonian matrix:

$$\hat{U}^\dagger \hat{H} \hat{U} = \hat{D}$$



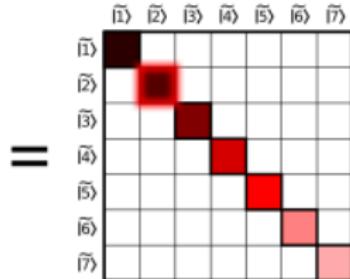
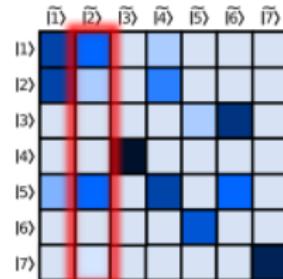
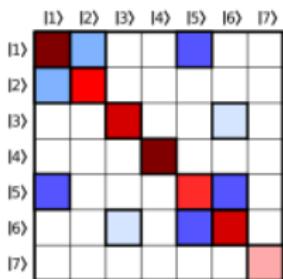
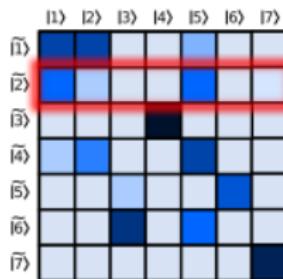
The **columns** of \hat{U} are **eigenvectors** of \hat{H} .

The **diagonal elements** of \hat{D} are **eigenvalues** of \hat{H} .

The Exciton Basis

Molecular eigenstates can be calculated by **diagonalizing** the Hamiltonian matrix:

$$\hat{U}^\dagger \hat{H} \hat{U} = \hat{D}$$



The **columns** of \hat{U} are **eigenvectors** of \hat{H} .

The **diagonal elements** of \hat{D} are **eigenvalues** of \hat{H} .

The Exciton Basis

Molecular eigenstates can be calculated by **diagonalizing** the Hamiltonian matrix:

$$\hat{U}^\dagger \hat{H} \hat{U} = \hat{D}$$

$ 1\rangle$	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$	$ 5\rangle$	$ 6\rangle$	$ 7\rangle$
Blue	Light Blue	White	Light Blue	White	White	Dark Blue
Light Blue	White	White	White	White	White	Dark Blue
White	White	White	White	White	White	Dark Blue
Light Blue	White	White	White	White	White	Dark Blue
White	White	White	White	White	White	Dark Blue
White	White	White	White	White	White	Dark Blue

$ 1\rangle$	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$	$ 5\rangle$	$ 6\rangle$	$ 7\rangle$
Dark Red	Light Blue	White	White	Light Blue	White	White
Light Blue	White	Red	White	White	White	White
White	White	Red	White	White	White	White
White	White	White	Dark Red	White	White	White
Light Blue	White	White	White	Red	Light Blue	White
White	White	White	White	White	Red	Light Red

$ 1\rangle$	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$	$ 5\rangle$	$ 6\rangle$	$ 7\rangle$
Dark Blue	Light Blue	White	Light Blue	White	White	Dark Blue
Light Blue	Dark Blue	White	White	White	White	Dark Blue
White	White	White	White	White	White	Dark Blue
White	White	White	White	White	White	Dark Blue
Light Blue	White	White	White	White	White	Dark Blue
White	White	White	White	White	White	Dark Blue

 $=$

$ 1\rangle$	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$	$ 5\rangle$	$ 6\rangle$	$ 7\rangle$
Dark Red	White	White	White	White	White	White
White	White	Dark Red	White	White	White	White
White	White	White	White	Dark Red	White	White
White	White	White	White	White	White	Dark Red
White	White	White	White	White	White	Light Red
White	White	White	White	White	Light Red	Light Red

The **columns** of \hat{U} are **eigenvectors** of \hat{H} .

The **diagonal elements** of \hat{D} are **eigenvalues** of \hat{H} .

We've seen previously that spectroscopic response functions are determined by the **eigenvalues** of \hat{H} and by the **transition dipole matrix elements** μ_{α}^{mn} between system eigenstates.

Question: We just calculated the eigenvalues of \hat{H} . How do we get μ_{α}^{mn} ?

Spectroscopic Calculations

We've seen previously that spectroscopic response functions are determined by the **eigenvalues** of \hat{H} and by the **transition dipole matrix elements** μ_{α}^{mn} between system eigenstates.

Question: We just calculated the eigenvalues of \hat{H} . How do we get μ_{α}^{mn} ?

Answer: Use the same transformation!

$$\mu_{\alpha}^{\tilde{m}\tilde{n}} = \left[\hat{U}^\dagger \hat{\mu}_{\alpha} \hat{U} \right]_{\tilde{m}\tilde{n}}$$

Example: Eigenvalues for the Excitonic Dimer

Consider a generic two-site model:

$$\hat{H} = \begin{bmatrix} -\Delta & v \\ v & \Delta \end{bmatrix}$$

Question: How do we find the eigenvalues?

Example: Eigenvalues for the Excitonic Dimer

Consider a generic two-site model:

$$\hat{H} = \begin{bmatrix} -\Delta & v \\ v & \Delta \end{bmatrix}$$

Question: How do we find the eigenvalues?

Answer: Set the determinant of $\hat{H} - \lambda \hat{1}$ equal to zero and solve for λ :

$$\begin{vmatrix} -\Delta - \lambda & v \\ v & \Delta - \lambda \end{vmatrix} = (-\Delta - \lambda)(\Delta - \lambda) - v^2$$

⇓

$$\lambda = \pm \sqrt{v^2 + \Delta^2}.$$

A Simple Example: The Excitonic Dimer

Consider a generic two-site model:

$$\hat{H} = \begin{bmatrix} -\Delta & v \\ v & \Delta \end{bmatrix}$$

Question: How do we find the eigenvectors?

A Simple Example: The Excitonic Dimer

Consider a generic two-site model:

$$\hat{H} = \begin{bmatrix} -\Delta & v \\ v & \Delta \end{bmatrix}$$

Question: How do we find the eigenvectors?

Answer: Plug in a value for λ and solve:

$$\lambda_{\pm} \begin{bmatrix} u_1^{(\pm)} \\ u_2^{(\pm)} \end{bmatrix} = \begin{bmatrix} -\Delta & v \\ v & \Delta \end{bmatrix} \begin{bmatrix} u_1^{(\pm)} \\ u_2^{(\pm)} \end{bmatrix} = \begin{bmatrix} -\Delta u_1^{(\pm)} + v u_2^{(\pm)} \\ v u_1^{(\pm)} + \Delta u_2^{(\pm)} \end{bmatrix}$$

gives

$$\mathbf{u}^{(\pm)} = \begin{bmatrix} \sin \theta_{\pm} \\ \cos \theta_{\pm} \end{bmatrix}$$

with

$$\tan \theta_{\pm} = \frac{v}{\Delta \pm \sqrt{\Delta^2 + v^2}}.$$

A Simple Example: The Excitonic Dimer

Consider a generic two-site model:

$$\hat{H} = \begin{bmatrix} -\Delta & v \\ v & \Delta \end{bmatrix}$$

Question: How do we find the dipole elements?

A Simple Example: The Excitonic Dimer

Consider a generic two-site model:

$$\hat{H} = \begin{bmatrix} -\Delta & v \\ v & \Delta \end{bmatrix}$$

Question: How do we find the dipole elements?

Answer: Transform the local-site dipoles!

$$\mu_{\alpha}^{\tilde{m}\tilde{n}} = [\hat{U}^\dagger \hat{\mu}_{\alpha} \hat{U}]_{\tilde{m}\tilde{n}} = \sum_{jk} U_{j\tilde{m}} U_{k\tilde{n}} \mu_{\alpha}^{j\tilde{k}}$$

Because ground and excited states don't mix:

$$\mu_{\alpha}^{\tilde{m}0} = [\hat{U}^\dagger \hat{\mu}_{\alpha} \hat{U}]_{\tilde{m}\tilde{n}} = \sum_{jk} U_{j\tilde{m}} U_{k0} \mu_{\alpha}^{j\tilde{k}} = \sum_j U_{j\tilde{m}} \mu_{\alpha}^{j0}.$$

The dipole moment transforms like a vector!