Molecular Excitons

Mike Reppert

November 12, 2020

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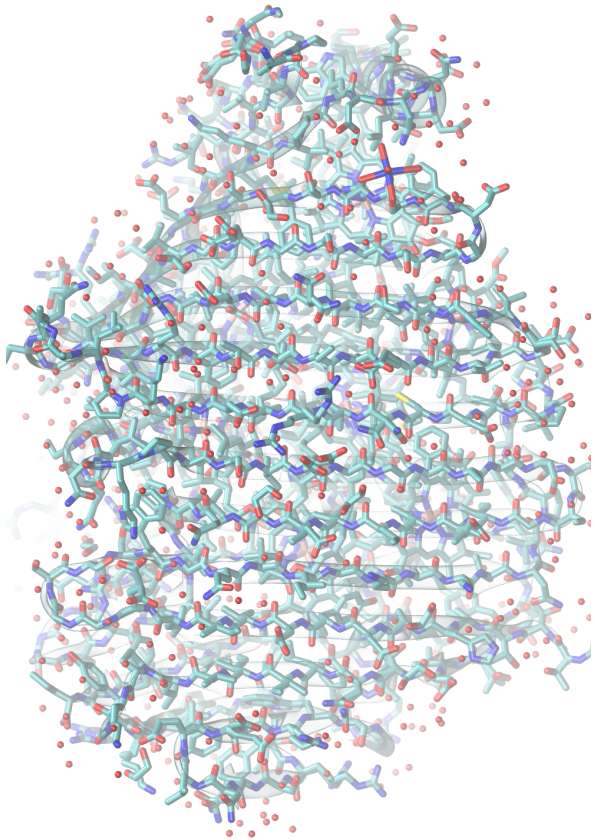
A **molecular exciton** is a delocalized excited state created by interactions between nearby molecules

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



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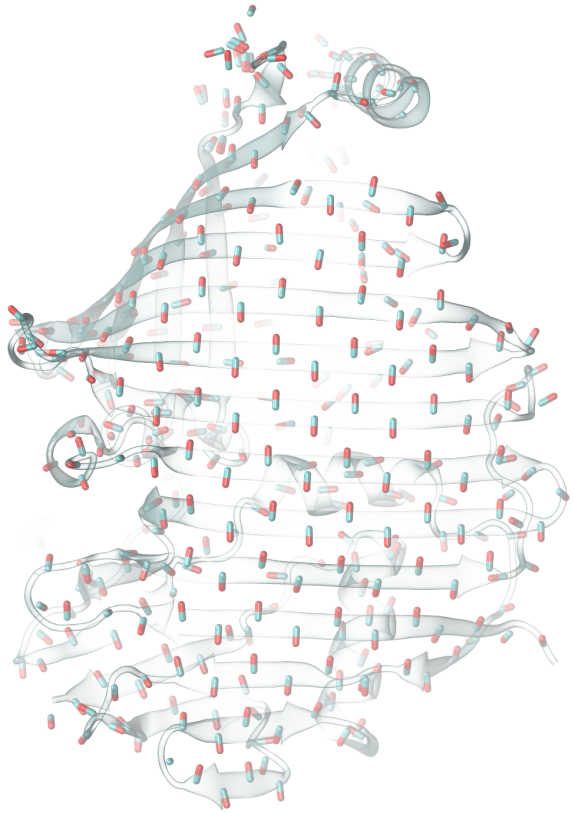

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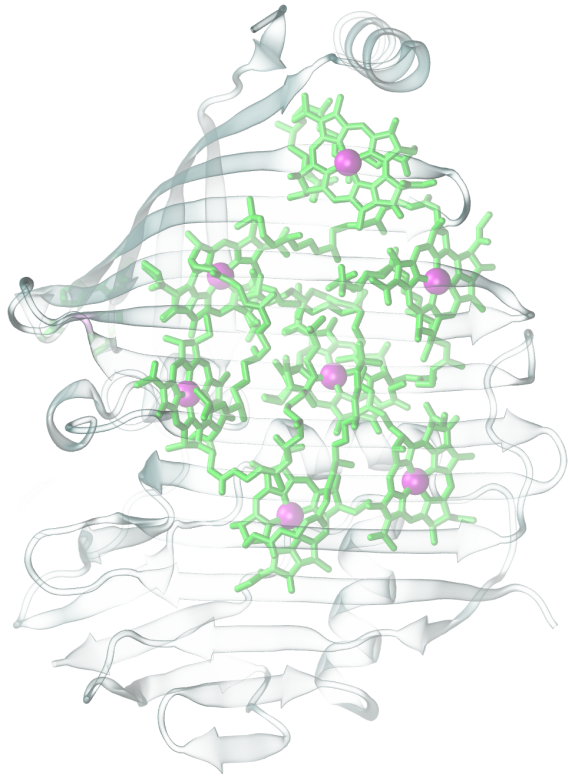
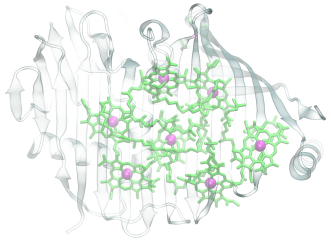


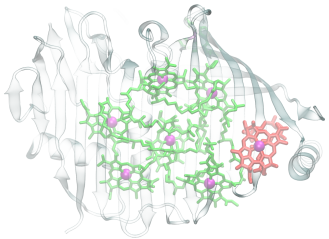
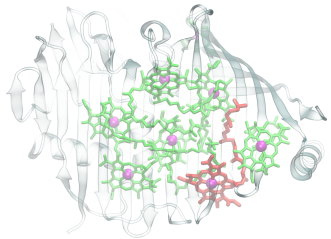
The Site Basis

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

Ground State:



Singly-Excited States: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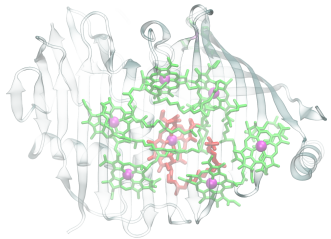
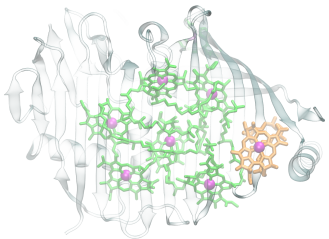
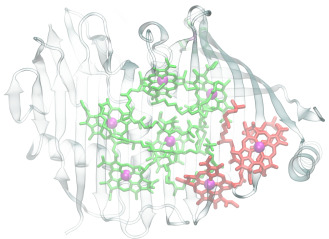


Multiply-Excited States: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The **site basis** is an orthonormal basis consisting of local-excitation wavefunctions:

Ground State:

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

Singly-Excited States:

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

$$\vdots$$

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

Multiply-Excited States:

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

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

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Ground State:

$$|0\rangle = |0, ..., 0\rangle$$

Singly-Excited States:

$$|1\rangle = |1, 0, ..., 0\rangle$$
$$\vdots$$
$$|n\rangle = |0, ..., 0, 1\rangle$$

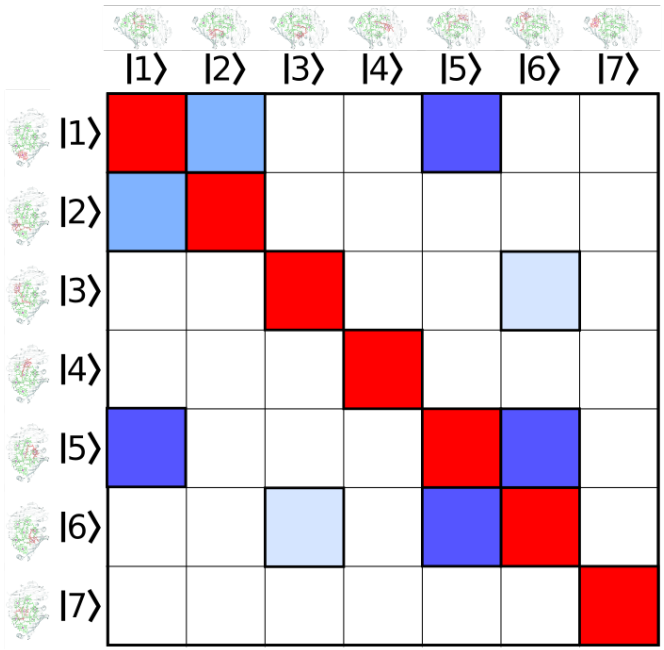
Multiply-Excited States:

$$|11\rangle = |2, 0, ..., 0\rangle$$

$$|12\rangle = |1, 1, 0, ..., 0\rangle$$
$$\vdots$$

The Site-Basis Hamiltonian

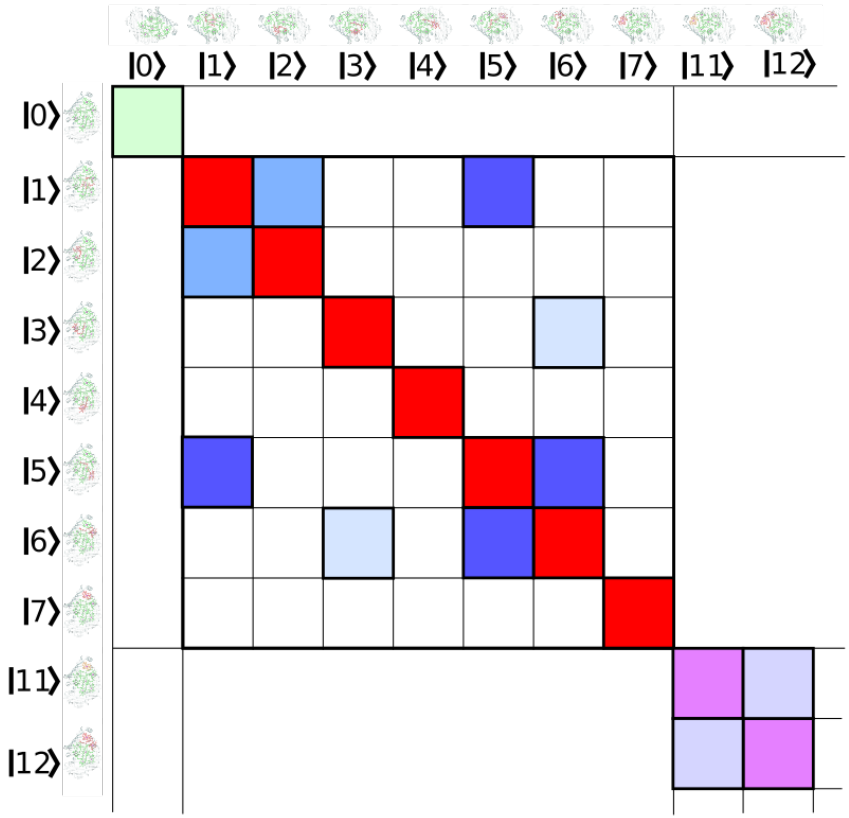
The **Hamiltonian matrix** for a molecular exciton system is obtained by taking matrix elements in a particular subspace, e.g., singly-excited states:



$$H_{mn} = \left\langle m \middle| \hat{H} \middle| n \right\rangle$$

Intra-Manifold Coupling

Hold up! What about inter-subspace interactions?



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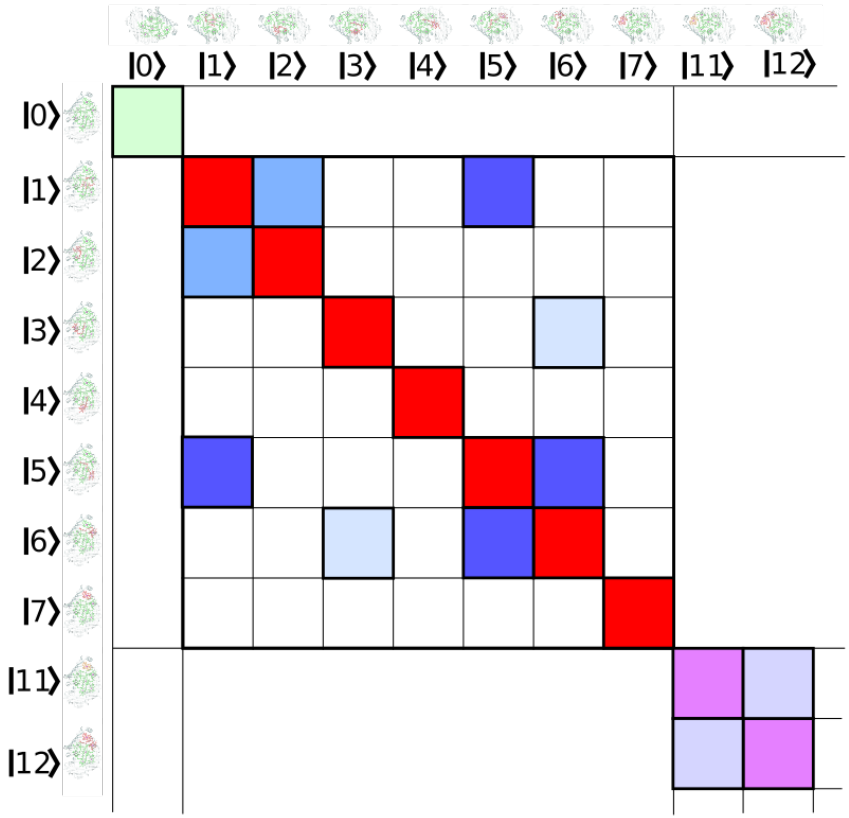
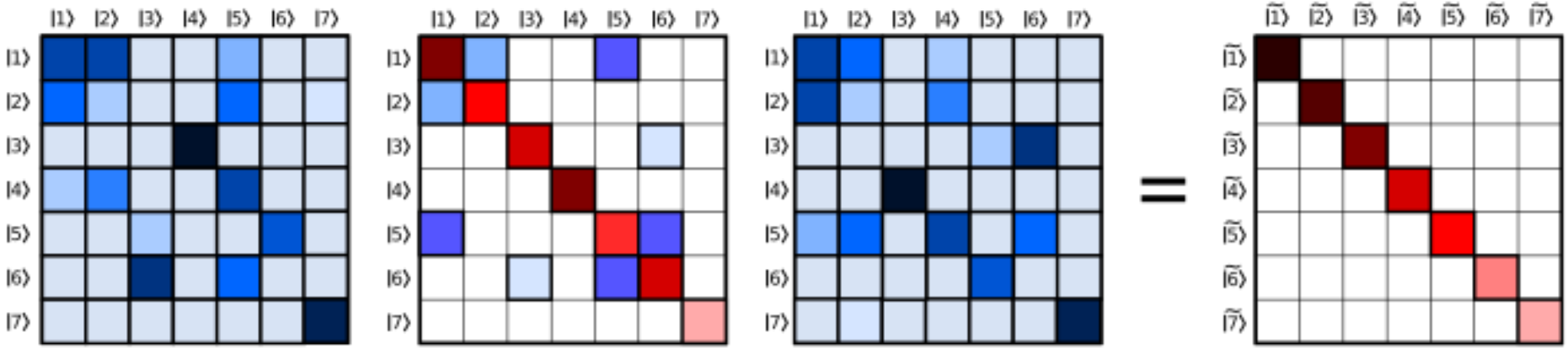


Answer: The **large energy differences** between excitation manifolds effectively weakens coupling!

The Exciton Basis

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

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



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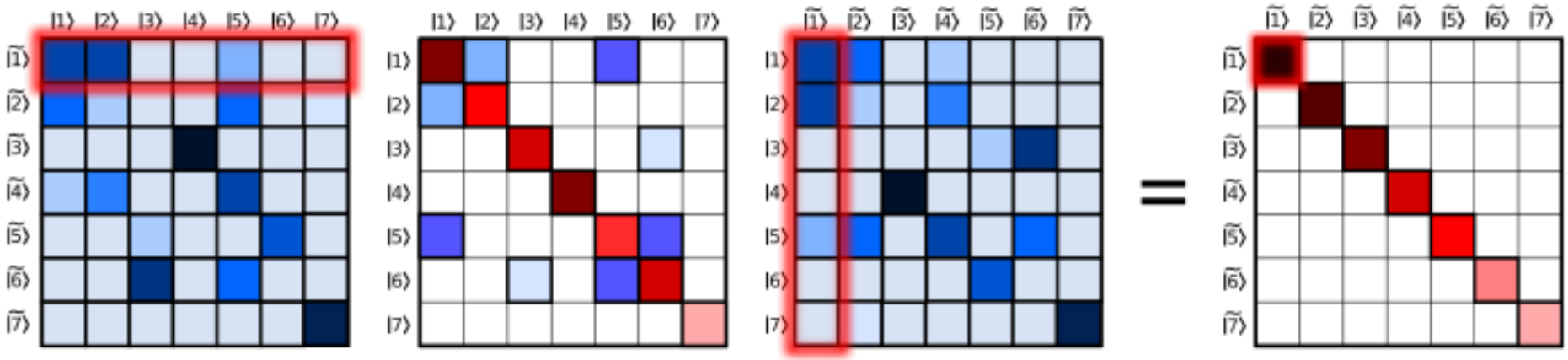

The **columns** of $\hat{U}$ are **eigenvectors** of $\hat{H}$.

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

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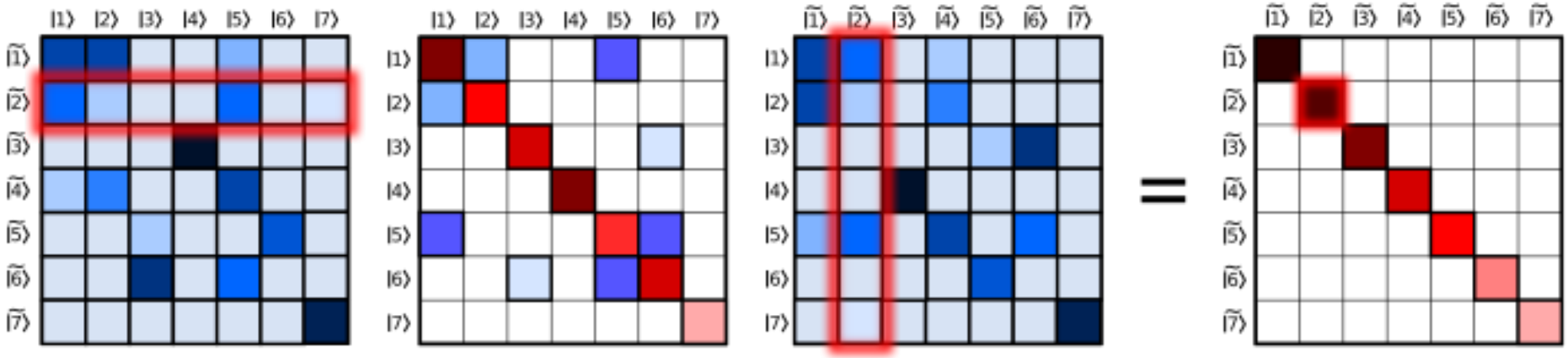

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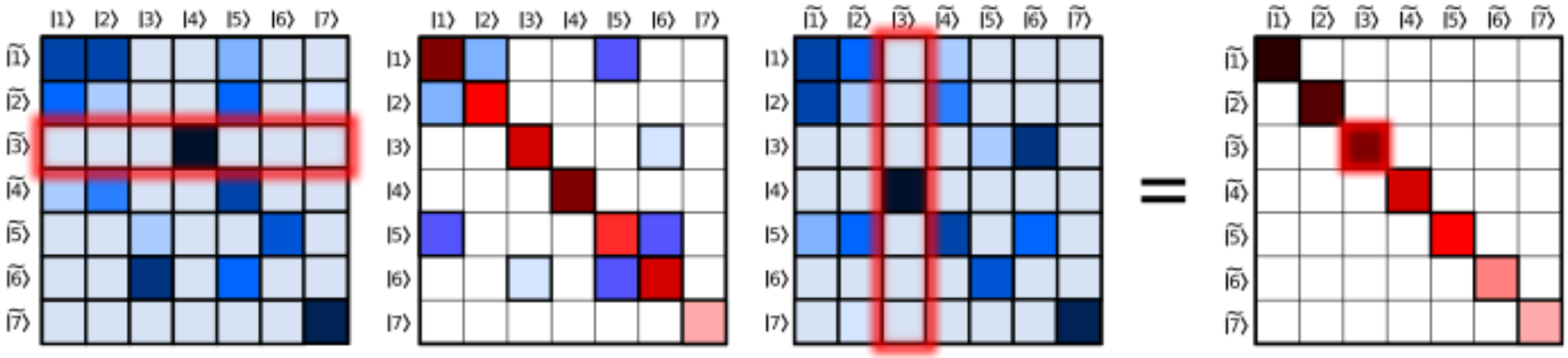

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Spectroscopic Calculations

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}?

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

Answer: Use the same transformation!

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

Dipole moment matrix elements

Since we're usually interested only in $0 \rightarrow \tilde{m}$ transitions:

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

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Key Point The dipole moment transforms like a vector!

Example: Eigenvalues for the Excitonic Dimer

Consider a generic two-site model:

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

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Question: How do we find the eigenvalues?

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

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

$$\Downarrow$$

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

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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

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

with

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

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Answer: Transform the local-site dipoles!

$$\mu_\alpha^{(\pm,0)} = \sin\theta_\pm \mu_\alpha^{10} + \cos\theta_\pm \mu_\alpha^{20}.$$