A One-Slide Summary of Quantum Mechanics

Fundamental Postulate:
\[ 0 \Psi = a \Psi \]
\( \Psi \) is an oracle!

Where does \( \Psi \) come from?

\( \Psi \) is refined

Variational Process

\[ \mathcal{H}\Psi = E \Psi \]

Energy (cannot go lower than "true" energy)

Convergence of \( E \)

truth

What if I can't converge \( E \)?

Test your oracle with a question to which you already know the right answer...
**Photoaffinity Labeling 1**

**ligand with attached photoaffinity label in enzyme active site**

![Chemical structure](image)

**singlet nitrene covalently modifies enzyme — active site can be identified by sequencing of protein**

![Chemical structure](image)
Attractive features of aromatic nitrenes as photoaffinity labels:
1) Generated with light outside of protein absorption bands
2) Highly reactive singlets
3) \( \text{N}_2 \) is an innocuous byproduct of activation

But:

Practical concern—must minimize

bond insertion

ISC to triplet state
(H-atom abstraction)

didehydroazepine
Photoaffinity Labeling 3

\[
\begin{align*}
\text{singlet} & \quad \text{bond insertion} \\
\text{didehydroazepine} & \quad \text{ISC to triplet state} \\
& \quad \text{(H-atom abstraction)}
\end{align*}
\]

\[
k_3 > k_1 > k_3 > k_1
\]

Platz et al.
Configuration Cartoons

$^3A_2$ (T0)

$^1A_2$ (S1)

$^1A_1$ (S2)

$^2A_1$ (S3)
Relative E (kcal/mol) for PhN

![PhN diagram]

<table>
<thead>
<tr>
<th></th>
<th>(^3!A_2)</th>
<th>(^1!A_2)</th>
<th>(^{1!}A_1)</th>
<th>(^{2!}A_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRCISD/DZP</td>
<td>0.0</td>
<td>21.0</td>
<td>39.8</td>
<td>(52)</td>
</tr>
<tr>
<td>CASPT2N(8,8)/TZP</td>
<td>0.0</td>
<td>19.3</td>
<td>34.8</td>
<td>54.5</td>
</tr>
<tr>
<td>CCSD(T)/DZP</td>
<td>0.0</td>
<td>—</td>
<td>35.2</td>
<td>(47.2)</td>
</tr>
<tr>
<td>BLYP/TZP</td>
<td>0.0</td>
<td>(14.3)</td>
<td>29.5</td>
<td>(41.0)</td>
</tr>
<tr>
<td>Expt.</td>
<td>0.0</td>
<td>18</td>
<td>30</td>
<td>?</td>
</tr>
</tbody>
</table>

Ring Expansion Mechanism

Wagner-Meerwein shift of CH to aligned in-plane (empty) N p orbital

The electronic configuration of the didehydroazepine correlates with the S3 nitrene
Avoided Crossing

\( \pi \)-Electron-donating groups should slow ring expansion

\[ \Delta E_1 ^ \dagger \quad \Delta E_2 ^ \dagger \]
Phenylnitrene Energies With 32 Different *meta* and *para* Substituents

![Graph showing Hammett σ vs. CASPT2 E_{rel}, kcal/mol for S1, S2, and S3 with some widening noted.](image)
Substituent Effects on Ring Expansion Coordinate

*Relative 298 K enthalpies in kcal/mol*

<table>
<thead>
<tr>
<th>Substituent</th>
<th>12.3</th>
<th>8.5</th>
<th>13.3</th>
<th>1.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHMe</td>
<td>8.5</td>
<td>2.7</td>
<td>5.8</td>
<td>-1.9</td>
</tr>
<tr>
<td>H</td>
<td>8.9</td>
<td>3.0</td>
<td>7.3</td>
<td>-1.6</td>
</tr>
<tr>
<td>F</td>
<td>9.5</td>
<td>3.7</td>
<td>4.8</td>
<td>-0.7</td>
</tr>
<tr>
<td>NO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Photoaffinity Labeling 4


$k_3$: $\text{singlet didehydroazepine}$
Theoretical Recommendation

Optimal photoaffinity labels will be aromatic azides combining steric bulk at ortho positions with strong electron-donating group at para position.
Generally good conduction because of significant overlap between HOMO of organic wire and filled metallic bands
Less well characterized—what do the virtual orbitals of the organic wire look like?
Experimental Method to Characterize Virtual Orbitals

Two-photon photoelectron spectroscopy (2PPE)

If there is an orbital below the vacuum level, that the electron temporarily occupies after a one-quantum absorption, then the kinetic energy from absorption of the second quantum scales exactly as the increase in the laser frequency.

If there is an orbital above the vacuum level, that the electron temporarily occupies after a two-quantum absorption (a so-called "resonance"), then the kinetic energy of the electron after detachment is independent of laser frequency.

If the excitation involves a direct two quantum absorption, the kinetic energy of the detected photoelectrons increases as twice the increase in laser frequency.
2PPE Example: Phenylthiolate on Copper

3.7 eV Photons

After covering the surface with an organic monolayer, a copper surface state disappears, and two new peaks are observed.
Phenylthiolate on Copper: Effect of Altered Photon Energies

Peak B moves, but Peak A does not
Peak Positions as a Function of Photon Energies

The spectra are essentially identical for three different thiolate coverages:

A corresponds to a resonance above the vacuum level (slope = 0)

B corresponds to a virtual orbital below the vacuum level (slope = 1)

What orbitals would be unaffected by the change of phenyl to ethyl to octyl?

Notice that the point of intersection of the two lines corresponds to the energy difference between the virtual orbitals (3.1 eV)
Computed Properties of Phenyl- and Propylthiolate

\[ \text{B3LYP/pVDZ+, units of eV, vertical properties} \]

\[ \begin{align*}
1^2A''(+) & \iff 1^1A' \\
\text{Ionization Potential} \\
2^2A^-(+) & \iff 1^1A' \\
\text{Electron Affinity} \\
7.3 & \text{ } -1.3 & 1.1 \\
7.9 & \text{ } -1.0 & 1.3 \\
\end{align*} \]
Orbitales de Fenil- y Propiltiolato de Calculación

son similarísimo

HOMO
symetría-π

LUMO
σ^*_{CuS}

LUMO+1
σ^*_{CS}
Improving the Surface Model

Little energetic difference between the two stereoisomers

The important orbitals are qualitatively the same as for the case with only one copper

The differences between LUMO and LUMO+1 in the two systems are 2.9 and 3.1 eV—in perfect accord with experiment (3.1 eV)

~15 kcal mol\(^{-1}\) higher in energy
Conclusions

1. The orbitals observed in the 2PPE experiment are the LUMO and LUMO+1 (\(\sigma^*_{\text{CuS}}\) and \(\sigma^*_{\text{CS}}\)) of the thiolate. These orbitals are below and above the vacuum level, respectively, and are qualitatively independent of the thiolate R group.

2. In addition, these orbitals fail to delocalize significantly off the Cu–S–C fragment. Thus, one assumes they will not facilitate conduction across an organic chain. This contrasts with the situation for the HOMO (used in hole transport) which is well delocalized.

3. Thiolates prefer to coordinate between two atoms of copper (side-on) rather than face on to a triangle of three surface atoms. The characters of the virtual orbitals localized on the organic fragment are not much affected by the presence of additional metal atoms.
Final Exam

• 10:30 to 12:30 Wednesday, May 10

• A–L 375 Science Classroom Bldg
M–Z 331 Smith Hall

• CJC Office Hours today 2-3 PM 221
Smith Hall