

Lecture 3

Many-electron systems and the Pauli principle

Potential energy of electrons and nuclei; Born-Oppenheimer approximation; Hartree product; Pauli exclusion; Slater determinants

Prof. David A. Kofke

CE 500 – Modeling Potential-Energy Surfaces

Department of Chemical & Biological Engineering

University at Buffalo

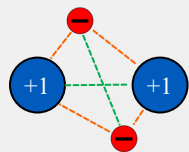


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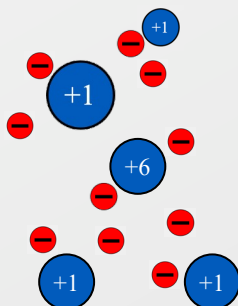
The potential energy for a system of electrons and nuclei is a sum of Coulomb terms

- Electrons + nuclei = (atom, molecule, or molecules)



H₂

Not to scale!



CH₄

Sum of Laplacians applied to each nuclear and electron coordinate

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 + V$$

$$V = V_{\text{NN}}^{\text{Coul}} + V_{\text{eN}}^{\text{Coul}} + V_{\text{ee}}^{\text{Coul}}$$

Potential is pairwise sum of Coulomb interactions

$$V_{\text{NN}}^{\text{Coul}} = + \sum_{A < B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{A,B}}$$

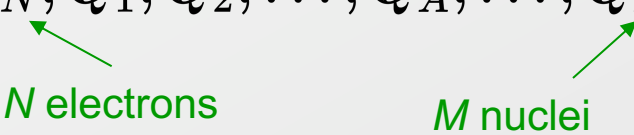
$$V_{\text{eN}}^{\text{Coul}} = - \sum_A \sum_i \frac{Z_A e^2}{4\pi\epsilon_0 r_{i,A}}$$

$$V_{\text{ee}}^{\text{Coul}} = + \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{i,j}}$$

In “atomic units”, \hbar , e , $4\pi\epsilon_0$, and m_e are each defined to be unity

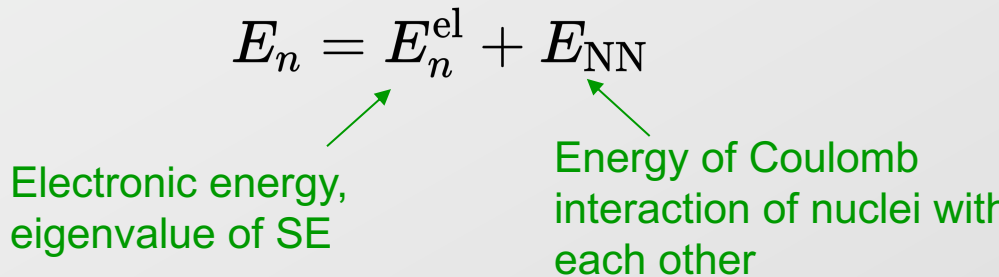
A system of electrons and nuclei are described by a single multivariate wavefunction

$$\begin{aligned}\psi &= \psi(\tau_1, \tau_2, \dots, \tau_i, \dots, \tau_N, Q_1, Q_2, \dots, Q_A, \dots, Q_M) \\ &= \psi(\tau^{(N)}, Q^{(M)})\end{aligned}$$


N electrons *M* nuclei

- Focus is on solution of Schrödinger equation for electrons in electrostatic potential of nuclei as fixed in space (“clamped”)
- Then total energy is sum of electronic and nuclear terms

$$E_n = E_n^{\text{el}} + E_{\text{NN}}$$


Electronic energy, eigenvalue of SE Energy of Coulomb interaction of nuclei with each other

$$\sum_{A < B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{A,B}}$$

The Born-Oppenheimer approximation separates electronic and nuclear degrees of freedom

- Electronic energy solved for a fixed set of nuclear positions

$$E_n^{\text{el}} = E_n^{\text{el}}(Q_1, \dots, Q_M) \quad \psi(\tau^{(N)}, Q^{(M)}) \approx \psi_e(\tau^{(N)}; Q^{(M)}) \psi_N(Q^{(M)})$$

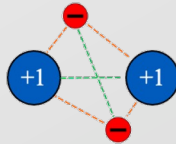
$m_e \ll m_N$

- Electronic SE: $\hat{H}_e \psi_e = E^{\text{el}} \psi_e$
- The dependence of E_n^{el} on $Q^{(M)}$ has the effect of introducing forces on the nuclei, in addition to their mutual Coulomb forces
- Together these forces on the nuclei define the adiabatic potential-energy surface, which governs their motion
 - Nuclear motion can be treated classically or quantum mechanically, as a separate issue

The *Hartree product* estimates ψ_e via a product of 1-electron orbitals. It is incorrect, but instructive

$$\psi_e(\tau_1, \tau_2, \dots, \tau_N) \approx \prod_{i=1}^N \varphi_i(\tau_i)$$

- The φ_i may be H-atom orbitals, but need not be
- They can be selected to attempt to best approximate ψ_e
- This model implies that the probability to find an electron at position r_i is independent of the positions of the other electrons, even though they have repulsive interactions



$$\psi^*(\tau^{(N)})\psi(\tau^{(N)}) = \underbrace{(\varphi_1^*(\tau_1)\varphi_1(\tau_1))}_{\text{Probability electron 1 at } \tau_1} \underbrace{(\varphi_2^*(\tau_2)\varphi_2(\tau_2))}_{\text{Probability electron 2 at } \tau_2} \dots \underbrace{(\varphi_N^*(\tau_N)\varphi_N(\tau_N))}_{\text{Probability electron N at } \tau_N}$$

×
×
×

Probability of configuration

- This is unrealistic, but there's a bigger problem...

The *Pauli principle* imposes a strict (anti-)symmetry on the wavefunction

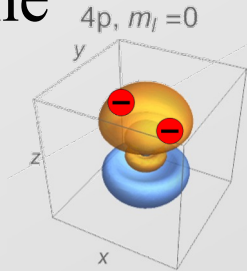
- First, swapping the identities of indistinguishable particles cannot change the probability of the configuration

$$\psi^*(1, 2)\psi(1, 2) = \psi^*(2, 1)\psi(2, 1)$$

Note: $\psi(1,2) \equiv \psi(\tau_1, \tau_2)$

- In particular, for electrons (and fermions in general) the wavefunction is antisymmetric (Pauli principle)

$$\psi(1, 2) = -\psi(2, 1)$$



- If 1 and 2 are in the same state, $\psi(1,2) = \psi(2,1)$. In such a case, both this and the Pauli principle can be true only if $\psi(1,2) = 0$.

– *Pauli exclusion principle*: any 2 electrons must occupy different states

The simple Hartree product does not satisfy the Pauli principle for indistinguishable particles

- If

$$\psi_e(1, 2, \dots, N) = \varphi_1(1)\varphi_2(2) \dots \varphi_N(N)$$

Note: $\varphi(1) \equiv \varphi(\tau_1)$

then, if $\varphi_1 \neq \varphi_2$, ψ_e does not satisfy the requirement for indistinguishable particles:

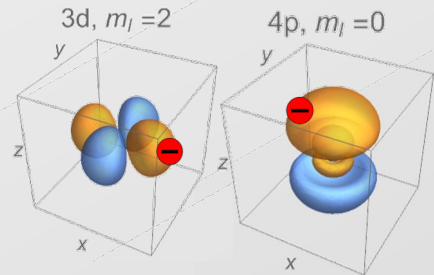
$$\varphi_1(1)\varphi_2(2) \dots \varphi_N(N) \neq \varphi_1(2)\varphi_2(1) \dots \varphi_N(N)$$

$\varphi_1(x_1, y_1, z_1)\varphi_2(x_2, y_2, z_2)$

$\varphi_1(x_2, y_2, z_2)\varphi_2(x_1, y_1, z_1)$


Alternatively, if, $\varphi_1 = \varphi_2$, ψ_e does not satisfy the Pauli principle

$$\varphi_2(1)\varphi_2(2) \dots \varphi_N(N) \neq -\varphi_2(2)\varphi_2(1) \dots \varphi_N(N)$$



We can formally define an “antisymmetrizer” operator to make Hartree product satisfy Pauli

$$\hat{\mathcal{A}} : \hat{\mathcal{A}}[\varphi_1(1)\varphi_2(2), \dots, \varphi_N(N)] = -\hat{\mathcal{A}}[\varphi_1(2)\varphi_2(1), \dots, \varphi_N(N)]$$

 antisymmetrizer operator

- Likewise for exchange of any two labels in product
- Generates a sum of $N!$ terms, so normalization requires a subsequent division by $(N!)^{1/2}$ (included with definition of operator)
- How can this be implemented in practice?

A Slater determinant forms an antisymmetric wavefunction from sums of Hartree products

- Determinant of matrix of 1-electron orbitals

$$\psi_e \approx \Phi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(N) & \varphi_2(N) & \cdots & \varphi_N(N) \end{vmatrix}$$

- Switching labels = switching rows
 - A property of determinant is that this will switch sign
- $N!$ terms \rightarrow division by $\sqrt{N!}$ means $\Phi^* \Phi$ will be normalized

Mathematica can be used to demonstrate some simple properties of determinants

swapping rows changes
sign of determinant

swapping columns changes
sign of determinant

adding a multiple of one
row/column to another does
not change determinant

```
nM = 4;  
M = RandomReal[10, {nM, nM}];  
MatrixForm@M  
Det[M]  
(*swap rows 1 & 3*)  
M[[{1, 3}]] = M[[{3, 1}]];  
MatrixForm@M  
Det[M]  
(*swap columns 1 & 3*)  
M[[All, {1, 3}]] = M[[All, {3, 1}]];  
MatrixForm@M  
Det[M]  
(*add half of row 2 to row 3*)  
M[[3]] += 0.5 M[[2]];  
MatrixForm@M  
Det[M]
```

```
{4.03924 4.80404 6.99246 3.87808  
 1.59 8.43131 2.25868 1.7121  
 5.30589 7.81292 9.49763 5.97595  
 1.80622 4.21877 6.29406 2.67081}
```

=
-63.8002

//MatrixForm=

→ {5.30589 7.81292 9.49763 5.97595
→ 1.59 8.43131 2.25868 1.7121
4.03924 4.80404 6.99246 3.87808
1.80622 4.21877 6.29406 2.67081}

=
63.8002

//MatrixForm=

↓ {9.49763 7.81292 5.30589 5.97595
2.25868 8.43131 1.59 1.7121
6.99246 4.80404 4.03924 3.87808
6.29406 4.21877 1.80622 2.67081}

=
-63.8002

//MatrixForm=

→ {9.49763 7.81292 5.30589 5.97595
→ 2.25868 8.43131 1.59 1.7121
8.1218 9.0197 4.83425 4.73414
6.29406 4.21877 1.80622 2.67081}

=
-63.8002

Consider Slater determinant for 2-electron, 2-orbital system

$$\begin{aligned}\Phi(1, 2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) \\ \varphi_1(2) & \varphi_2(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2))\end{aligned}$$

- Switch electron labels

$$\begin{aligned}\Phi(2, 1) &= \frac{1}{\sqrt{2}} (\varphi_1(2)\varphi_2(1) - \varphi_2(2)\varphi_1(1)) \\ &= -\Phi(1, 2)\end{aligned}$$

obeys Pauli principle!

Mathematica can be used to construct a Slater determinant of orbitals for arbitrary n

```
(* This defines a wavefunction  $\psi$  as a Slater determinant
of nM orbital functions *)

Clear[ $\psi$ , M]
nM = 4;
tauList0 = ToExpression[" $\tau$ " <> ToString[#] & /@ Range[nM]]
M = Table[ $\phi_i$ [tauList0[[j]]], {j, nM}, {i, nM}];
MatrixForm@M (* Just to see what M looks like *)

 $\psi$ [tau_List] := With[{n = Length[tau]},

$$\frac{1}{\text{Sqrt}[n!]} \text{Det}\left[\text{Table}[\phi_i[\text{tau}[[j]]], \{j, n\}, \{i, n\}]\right]$$

M
(*Note distinction between the list "tau" and its elements  $\tau_i$ *)

 $\psi$ [tauList0]
Length[Expand@%]

(* This defines a list that permutes some of the arguments *)
tauList1 = Permute[tauList0, Cycles@{{1, 2}}]

(* If this is zero, then the permutation(s) changes the sign
of the wavefunction. This happens for an odd number of
permutations *)
```

```
 $\psi$ [tauList0] +  $\psi$ [tauList1] // Simplify
```

{ τ_1 , τ_2 , τ_3 , τ_4 } tauList0

MatrixForm=

$$M = \begin{pmatrix} \phi_1[\tau_1] & \phi_2[\tau_1] & \phi_3[\tau_1] & \phi_4[\tau_1] \\ \phi_1[\tau_2] & \phi_2[\tau_2] & \phi_3[\tau_2] & \phi_4[\tau_2] \\ \phi_1[\tau_3] & \phi_2[\tau_3] & \phi_3[\tau_3] & \phi_4[\tau_3] \\ \phi_1[\tau_4] & \phi_2[\tau_4] & \phi_3[\tau_4] & \phi_4[\tau_4] \end{pmatrix}$$

$$\Psi = \frac{1}{2\sqrt{6}} (\phi_1[\tau_4] \phi_2[\tau_3] \phi_3[\tau_2] \phi_4[\tau_1] - \phi_1[\tau_3] \phi_2[\tau_4] \phi_3[\tau_2] \phi_4[\tau_1] - \phi_1[\tau_4] \phi_2[\tau_2] \phi_3[\tau_3] \phi_4[\tau_1] + \phi_1[\tau_2] \phi_2[\tau_4] \phi_3[\tau_3] \phi_4[\tau_1] + \phi_1[\tau_3] \phi_2[\tau_2] \phi_3[\tau_4] \phi_4[\tau_1] - \phi_1[\tau_2] \phi_2[\tau_3] \phi_3[\tau_4] \phi_4[\tau_1] - \phi_1[\tau_4] \phi_2[\tau_3] \phi_3[\tau_1] \phi_4[\tau_2] + \phi_1[\tau_3] \phi_2[\tau_4] \phi_3[\tau_1] \phi_4[\tau_2] + \phi_1[\tau_4] \phi_2[\tau_1] \phi_3[\tau_3] \phi_4[\tau_2] - \phi_1[\tau_1] \phi_2[\tau_4] \phi_3[\tau_3] \phi_4[\tau_2] - \phi_1[\tau_3] \phi_2[\tau_1] \phi_3[\tau_4] \phi_4[\tau_2] + \phi_1[\tau_1] \phi_2[\tau_3] \phi_3[\tau_4] \phi_4[\tau_2] + \phi_1[\tau_4] \phi_2[\tau_2] \phi_3[\tau_1] \phi_4[\tau_3] - \phi_1[\tau_2] \phi_2[\tau_4] \phi_3[\tau_1] \phi_4[\tau_3] - \phi_1[\tau_4] \phi_2[\tau_1] \phi_3[\tau_2] \phi_4[\tau_3] + \phi_1[\tau_1] \phi_2[\tau_4] \phi_3[\tau_2] \phi_4[\tau_3] + \phi_1[\tau_2] \phi_2[\tau_1] \phi_3[\tau_4] \phi_4[\tau_3] - \phi_1[\tau_1] \phi_2[\tau_2] \phi_3[\tau_4] \phi_4[\tau_3] - \phi_1[\tau_3] \phi_2[\tau_2] \phi_3[\tau_1] \phi_4[\tau_4] + \phi_1[\tau_2] \phi_2[\tau_3] \phi_3[\tau_1] \phi_4[\tau_4] + \phi_1[\tau_3] \phi_2[\tau_1] \phi_3[\tau_2] \phi_4[\tau_4] - \phi_1[\tau_1] \phi_2[\tau_3] \phi_3[\tau_2] \phi_4[\tau_4] - \phi_1[\tau_2] \phi_2[\tau_1] \phi_3[\tau_3] \phi_4[\tau_4] + \phi_1[\tau_1] \phi_2[\tau_2] \phi_3[\tau_3] \phi_4[\tau_4])$$

24 Number of terms

{ τ_2 , τ_1 , τ_3 , τ_4 } tauList1

0 $\Psi(\text{original}) + \psi(\text{permuted})$

Each term in ψ has each τ and each ϕ exactly once

Suggested Reading/Viewing

- Autschbach Ch. 7