Lecture 4
Electron Repulsion Integrals and Exchange

Orthogonal functions; energy expectation for Slater determinants; exchange

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A mathematical aside

Orthogonal vectors are perpendicular. Their dot product is zero

```
(* Three random vectors in a 3D space *)
v = (2 {Random[], Random[], Random[]} - 1) & /@ Range[3]
```

```
{{0.961041, 0.445121, -0.558889},
 {0.306363, 0.775806, -0.934734}, {0.0609626, 0.128556, 0.00805399}}
```

```
v[[1]]
```

```
{0.961041, 0.445121, -0.558889}
```

```
(* Show that they aren't normalized or orthogonal *)
Table[v[[i]].v[[j]], {i, 3}, {j, 3}] // TableForm
```

ableForm=

1.43409	1.16217	0.111309
1.16217	1.56946	0.110883
0.111309	0.110883	0.0203079

$$\begin{pmatrix} \mathbf{v}_1 \cdot \mathbf{v}_1 & \mathbf{v}_1 \cdot \mathbf{v}_2 & \mathbf{v}_1 \cdot \mathbf{v}_3 \\ \mathbf{v}_2 \cdot \mathbf{v}_1 & \mathbf{v}_2 \cdot \mathbf{v}_2 & \mathbf{v}_2 \cdot \mathbf{v}_3 \\ \mathbf{v}_3 \cdot \mathbf{v}_1 & \mathbf{v}_3 \cdot \mathbf{v}_2 & \mathbf{v}_3 \cdot \mathbf{v}_3 \end{pmatrix}$$

```
(* Normalize them *)
v = Normalize /@ v
```

```
{{0.802516, 0.371698, -0.466699},
 {0.244546, 0.619267, -0.746127}, {0.42779, 0.902109, 0.056517}}
```

```
(* Visualize them *)
arrows = Arrow[{{0, 0, 0}, #}] & /@ v;
originalImage = Graphics3D[arrows, PlotRange → {{-1, 1}, {-1, 1}, {-1, 1}}]
```

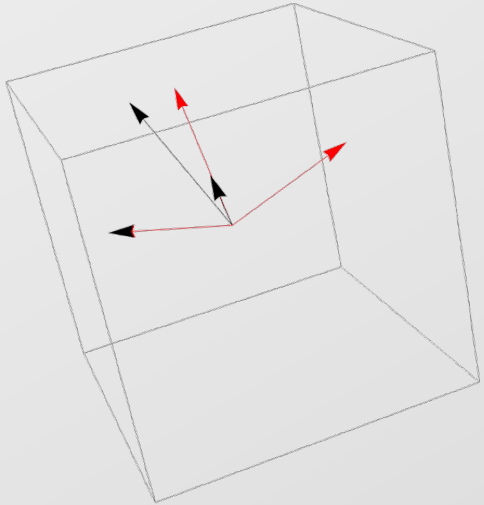
```
(* Make them orthogonal *)
ov = Orthogonalize[v]
Table[ov[[i]].ov[[j]], {i, 3}, {j, 3}] // Chop // TableForm
```

```
{{0.802516, 0.371698, -0.466699},
 {-0.596345, 0.523935, -0.608166}, {0.0184661, 0.766377, 0.642126}}
```

TableForm=

1.	0	0
0	1.	0
0	0	1.

```
oarrows = Arrow[{{0, 0, 0}, 0.99 #}] & /@ ov;
orthogonalImage = Graphics3D[{Red, oarrows}, PlotRange → {{-1, 1}, {-1, 1}, {-1, 1}}];
Show[originalImage, orthogonalImage]
```



Rotate view in Mathematica

Functions are vectors in an ∞-dimensional space. They also can be orthonormal

- Vector $\mathbf{v}_i \rightarrow \mathbf{v}(i) \rightarrow \mathbf{v}(x)$ (function)
  - Continuous index (x) instead of integer index (i)
- "Dot product" sums/integrates over index

$$\mathbf{v} \cdot \mathbf{w} = \mathbf{v}^{\mathrm{T}}\mathbf{w} = \sum_i \mathbf{v}_i \mathbf{w}_i \rightarrow \langle f|g \rangle = \int f^*(x) g(x) dx$$

  - Integral is over domain of x, which may be multivariate
- Normalized function $\langle f|f \rangle = 1$
- Orthogonal functions $\langle f|g \rangle = 0$

The Gram-Schmidt process can provide a set of orthogonal functions from a non-orthogonal set

Gram-Schmidt process

```
[3990]:= (* Define inner product *)
         Clear[BraKet]
         BraKet[{f_}, {g_}] := Integrate[f[x]*g[x], {x, 0, 1}]

[3971]:= (* original functions *)
         nx = 3;
         Clear[f]
         f[1][x_] := 1
         f[2][x_] := x
         f[3][x_] := x^2

         (* test for orthonormal *)

[3932]:= TableForm@Table[BraKet[{f[i]}, {f[j]}], {i, 1, nx}, {j, 1, nx}]
```

ut[3932]//TableForm=

1	$\frac{1}{2}$	$\frac{1}{3}$
$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$
$\frac{1}{3}$	$\frac{1}{4}$	$\frac{1}{5}$

```
(* Generate new, orthonormal set *)
(* First function is same as original set, but normalized *)
Clear[g]
g[1][x_] := Release[ f[1][x] / Sqrt@BraKet[{f[1]}, {f[1]}] ]
(* Subtract of1 component *)
g[2][x_] := Release[f[2][x] - BraKet[{g[1]}, {f[2]}]*g[1][x] ]
(* Normalize *)
g[2][x_] := Release[ g[2][x] / ⟨g[2]|g[2]⟩^(1/2) ]
```

$g_1 = f_1 / \langle f_1 | f_1 \rangle^{1/2}$

$g_2 = f_2 - \langle g_1 | f_2 \rangle g_1$

Normalize

<esc>braket<esc>

```
d of2 components *)
g[3][x_] := Release[f[3][x] - ⟨g[1]|f[3]⟩ g[1][x]
                            - ⟨g[2]|f[3]⟩ g[2][x] ]
(* Normalize *)
g[3][x_] := Release[Simplify[ g[3][x] / ⟨g[3]|g[3]⟩^(1/2) ]]
```

$g_3 = f_3 - \langle g_1 | f_3 \rangle g_1 - \langle g_2 | f_3 \rangle g_2$

Normalize

```
(* Test for orthonormal *)
TableForm@Table[BraKet[{g[i]}, {g[j]}], {i, 1, nx}, {j, 1, nx}]
```

'/TableForm=

1	0	0
0	1	0
0	0	1

```
(* Look at the orthonormal set *)
g[#][x] & /@ Range[3] // TableForm
```

'/TableForm=

1

$2\sqrt{3}\left(-\frac{1}{2}+x\right)$

$\sqrt{5}\left(1-6x+6x^2\right)$

The orbitals for the hydrogen-like atom are orthonormal

```
BraKet[{f1_}, {f2_}] := Integrate[f1[r, θ, ϕ]* × f2[r, θ, ϕ] Sin[θ] r^2, {ϕ, 0, 2 Pi},
  {θ, 0, Pi}, {r, 0, Infinity}]

With[{state1 = {1, 0, 0}, state2 = {1, 0, 0}, Z1 = 1, Z2 = 1},
 BraKet[{ψ[state1, {#1, #2, #3}, Z1] &}, {ψ[state2, {#1, #2, #3}, Z2] &}]]
```

This defines a 3-argument function, which is what this BraKet needs

```
1.00000000

With[{state1 = {2, 1, 0}, state2 = {2, 1, -1}, Z1 = 1, Z2 = 1},
 BraKet[{ψ[state1, {#1, #2, #3}, Z1] &}, {ψ[state2, {#1, #2, #3}, Z2] &}]]

0

(* With different Z, orbitals with unlike (nlm) are orthogonal
 but same (nlm) don't integrate to unity *)

With[{state1 = {2, 1, 0}, state2 = {2, 1, -1}, Z1 = 1, Z2 = 2},
 BraKet[{ψ[state1, {#1, #2, #3}, Z1] &}, {ψ[state2, {#1, #2, #3}, Z2] &}]]
With[{state1 = {2, 1, 0}, state2 = {2, 1, 0}, Z1 = 1, Z2 = 2},
 ⟨ψ[state1, {#1, #2, #3}, Z1] & | ψ[state2, {#1, #2, #3}, Z2] &⟩]

0

0.74493554
```

```
table =
  Flatten[
   Table[{n1, l1, m1, n2, l2, m2,
     With[{state1 = {n1, l1, m1}, state2 = {n2, l2, m2}, Z1 = 1, Z2 = 1},
      ⟨ψ[state1, {#1, #2, #3}, Z1] & | ψ[state2, {#1, #2, #3}, Z2] &⟩]},
    {n1, 1, 2}, {n2, 1, n1}, {l1, 0, n1 - 1}, {l2, 0, n2 - 1},
    {m1, -l1, l1}, {m2, -l2, l2}], 5];
TableForm[table, TableHeadings → {None, {n1, l1, m1, n2, l2, m2, "<ψ1 | ψ2>"}}]
```

/TableForm=

n_1	l_1	m_1	n_2	l_2	m_2	$\langle\psi_1 \mid \psi_2\rangle$
1	0	0	1	0	0	1.00000000
2	0	0	1	0	0	0
2	1	-1	1	0	0	0
2	1	0	1	0	0	0
2	1	1	1	0	0	0
2	0	0	2	0	0	1.0000000
2	0	0	2	1	-1	0
2	0	0	2	1	0	0
2	0	0	2	1	1	0
2	1	-1	2	0	0	0
2	1	0	2	0	0	0
2	1	1	2	0	0	0
2	1	-1	2	1	-1	1.00000000
2	1	-1	2	1	0	0
2	1	-1	2	1	1	0
2	1	0	2	1	-1	0
2	1	0	2	1	0	1.00000000
2	1	0	2	1	1	0
2	1	1	2	1	-1	0
2	1	1	2	1	0	0
2	1	1	2	1	1	1.00000000

End of aside

We define an abstract BraKet notation that captures its basic properties, including orbital orthonormality

```
(* Linearity of <f|g> *)
BraKet[{f_ + g_}, {k_}] := BraKet[{f}, {k}] + BraKet[{g}, {k}]
BraKet[{f_}, {i_ + k_}] := BraKet[{f}, {i}] + BraKet[{f}, {k}]
BraKet[{c_ ? NumericQ f_}, {g_}] := c BraKet[{f}, {g}]
BraKet[{f_}, {c_ ? NumericQ g_}] := c BraKet[{f}, {g}]
BraKet[{f_[x_] q_}, {g_[x_] r_}] := BraKet[{f[x]}, {g[x]}] × BraKet[{q}, {r}]

(* Linearity of <f|A|k> *)
BraCKet[{f_ + g_}, A_, {k_}] :=
 BraCKet[{f}, A, {k}] + BraCKet[{g}, A, {k}] // Simplify
BraCKet[{f_}, A_, {i_ + k_}] :=
 BraCKet[{f}, A, {i}] + BraCKet[{f}, A, {k}] // Simplify
BraCKet[{c_ ? NumericQ f_}, A_, {k_}] := c BraCKet[{f}, A, {k}] // Simplify
BraCKet[{f_}, A_, {c_ ? NumericQ k_}] := c BraCKet[{f}, A, {k}] // Simplify

(* Separation of products involving different variables *)
BraCKet[{f_[x_] q_}, A_[x_], {g_[x_] r_}] :=
 BraCKet[{f[x]}, A[x], {g[x]}] × BraKet[{q}, {r}]
BraCKet[{f_[x_] × i_[y_] q_}, A_[x_, y_], {g_[x_] × h_[y_] r_}] :=
 BraCKet[{f[x] × i[y]}, A[x, y], {g[x] × h[y]}] × BraKet[{q}, {r}]

(* Linearity with respect to operators *)
BraCKet[{f_}, A_ + B_, {g_}] := BraCKet[{f}, A, {g}] + BraCKet[{f}, B, {g}]
BraCKet[{f_}, c_ ? NumericQ A_, {g_}] := c BraCKet[{f}, A, {g}]
```

Transformation rules that can be applied when desired

```
(* Terms with different dummy indices are equivalent and can be summed *)
sumRules =
  {(c_ : 1) BraCKet[{f_[x_] × g_[y_]}, A_[x_, y_], {f_[x_] × g_[y_]}] +
     (d_ : 1) BraCKet[{f_[w_] × g_[z_]}, A_[z_, w_], {f_[w_] × g_[z_]}] :>
    (c + d) BraCKet[{f[x] × g[y]}, A[x, y], {f[x] × g[y]}],
(c_ : 1) BraCKet[{f_[x_] × g_[y_]}, A_[x_, y_], {f_[y_] × g_[x_]}] +
     (d_ : 1) BraCKet[{f_[w_] × g_[z_]}, A_[z_, w_], {f_[z_] × g_[w_]}] :>
    (c + d) BraCKet[{f[x] × g[y]}, A[x, y], {f[y] × g[x]}],
(c_ : 1) BraCKet[{f_[x_] × g_[y_]}, A_[x_, y_], {h_[x_] × i_[y_]}] +
     (d_ : 1) BraCKet[{f_[w_] × g_[z_]}, A_[w_, z_], {h_[w_] × i_[z_]}] :>
    (c + d) BraCKet[{f[x] × g[y]}, A[x, y], {h[x] × i[y]}],
(c_ : 1) BraCKet[{f_[x_]}, A_[x_], {g_[x_]}] +
     (d_ : 1) BraCKet[{f_[y_]}, A_[y_], {g_[y_]}] :>
    (c + d) BraCKet[{f[x]}, A[x], {g[x]}]
};

(* Orthonomality condition *)
orthonormalRule = {BraKet[{f_[x_]}, {g_[x_]}] :> If[f === g, 1, 0]};
```

These commands are provided in the MyBraKet.nb file

The energy expectation from a Slater determinant can separate into 0-, 1- and 2-electron contributions

- Energy expectation $\langle E \rangle = \left\langle \Phi | \hat{H} | \Phi \right\rangle$

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

- Remember the contributions to $\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V(r)$

$$V_{\mathrm{eN}}^{\mathrm{Coul}} = -\sum_A \sum_i \frac{Z_A e^2}{4\pi\epsilon_0 r_{i,A}} \qquad V_{\mathrm{ee}}^{\mathrm{Coul}} = +\sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{i,j}} \qquad V_{\mathrm{NN}}^{\mathrm{Coul}} = +\sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{A,B}}$$

$$\hat{H} = \sum_i \left(-\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 r_{i,A}} \right) + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{i,j}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{A,B}}$$

1-electron term, $\hat{h}_i$ | 2-electron term, $\hat{h}_{i,j}$ | 0-electron term

The 1-electron contribution to expectation energy with Slater determinant is unsurprising

Slater-determinant wavefunction

$$\langle E \rangle = \left\langle \Phi \middle| \sum_i \hat{h}_i \middle| \Phi \right\rangle + \left\langle \Phi \middle| \sum_{i<j} \hat{h}_{i,j} \middle| \Phi \right\rangle + V_{\mathrm{NN}}^{\mathrm{Coul}}$$

```
Φ[tau_List] := With[{n = Length[tau]},
  1/Sqrt[n!] Det[Table[ϕ_i[tau[[j]]], {i, n}, {j, n}]]]

nM = 2;   2 orbitals
tauList = Range[nM]   ID coordinate by number, dropping "τ", e.g., 1 rather than τ1
BraCKet[{Φ[tauList]}, Sum[h[i], {i, nM}], {Φ[tauList]}]
% //. orthonormalRule // Simplify
% //. noDummiesRule // Simplify
{1, 2}   List of coordinates, τ
```

Raw form of <Φ|Σh|Φ>

$$\frac{1}{2}\Big(\langle\phi_2[2]\,|\,h[2]\,|\,\phi_2[2]\rangle\langle\phi_1[1]\,|\phi_1[1]\rangle - \langle\phi_2[2]\,|\,h[2]\,|\,\phi_1[2]\rangle\langle\phi_1[1]\,|\phi_2[1]\rangle - \langle\phi_2[1]\,|\,h[1]\,|\,\phi_2[1]\rangle\langle\phi_1[2]\,|\phi_1[2]\rangle - \langle\phi_2[1]\,|\,h[1]\,|\,\phi_1[1]\rangle\langle\phi_1[2]\,|\phi_2[2]\rangle - \langle\phi_1[2]\,|\,h[2]\,|\,\phi_2[2]\rangle\langle\phi_2[1]\,|\phi_1[1]\rangle + \langle\phi_1[2]\,|\,h[2]\,|\,\phi_1[2]\rangle\langle\phi_2[1]\,|\phi_2[1]\rangle - \langle\phi_1[1]\,|\,h[1]\,|\,\phi_2[1]\rangle\langle\phi_2[2]\,|\phi_1[2]\rangle + \langle\phi_1[1]\,|\,h[1]\,|\,\phi_1[1]\rangle\langle\phi_2[2]\,|\phi_2[2]\rangle\Big)$$

After applying orthonormal rule

$$\frac{1}{2}\Big(\langle\phi_1[1]\,|\,h[1]\,|\,\phi_1[1]\rangle + \langle\phi_1[2]\,|\,h[2]\,|\,\phi_1[2]\rangle + \langle\phi_2[1]\,|\,h[1]\,|\,\phi_2[1]\rangle + \langle\phi_2[2]\,|\,h[2]\,|\,\phi_2[2]\rangle\Big)$$

Removed dummy integration variables

$$\langle\phi_1\,|\,h\,|\,\phi_1\rangle + \langle\phi_2\,|\,h\,|\,\phi_2\rangle$$

```
nM = 3;
tauList = Range[nM]
BraCKet[{Φ[tauList]}, Sum[h[i], {i, nM}], {Φ[tauList]}]
% //. orthonormalRule // Simplify
% //. noDummiesRule // Simplify
{1, 2, 3}
```

3 orbitals

$$\frac{1}{6}\Big(\mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_2[3]\}]\langle\phi_1[2]\,|\phi_3[2]\rangle\langle\phi_2[1]\,|\phi_1[1]\rangle - \mathrm{BraCKet}[\{\phi_3[2]\},h[2],\{\phi_3[2]\}]\langle\phi_1[3]\,|\phi_2[3]\rangle\langle\phi_2[1]\,|\phi_1[1]\rangle + \mathrm{BraCKet}[\{\phi_3[2]\},h[2],\{\phi_2[2]\}]\langle\phi_1[3]\,|\phi_3[3]\rangle\langle\phi_2[1]\,|\phi_1[1]\rangle - \mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_3[3]\}]\langle\phi_1[2]\,|\phi_2[2]\rangle\langle\phi_2[1]\,|\phi_1[1]\rangle + \mathrm{BraCKet}[\{\phi_3[2]\},h[2],\{\phi_3[2]\}]\langle\phi_1[3]\,|\phi_3[3]\rangle\langle\phi_2[1]\,|\phi_2[1]\rangle - \mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_3[3]\}]\langle\phi_1[2]\,|\phi_2[2]\rangle\langle\phi_2[1]\,|\phi_1[1]\rangle - \langle\phi_1[2]\,|\phi_2[2]\rangle\langle\phi_2[1]\,|\phi_1[1]\rangle\Big) - \mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_3[3]\}]\langle\phi_1[2]\,|\phi_1[2]\rangle\langle\phi_2[1]\,|\phi_3[1]\rangle + \mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_3[1]\}]\langle\phi_1[2]\,|\phi_2[2]\rangle\langle\phi_2[1]\,|\phi_3[1]\rangle - \mathrm{BraCKet}[\{\phi_3[2]\},h[2],\{\phi_2[2]\}]\langle\phi_1[3]\,|\phi_3[3]\rangle\langle\phi_2[1]\,|\phi_3[1]\rangle + \mathrm{BraCKet}[\{\phi_3[2]\},h[2],\{\phi_3[2]\}]\langle\phi_1[3]\,|\phi_2[3]\rangle\langle\phi_2[1]\,|\phi_3[1]\rangle + \mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_3[3]\}]\langle\phi_1[1]\,|\phi_3[1]\rangle\langle\phi_2[2]\,|\phi_1[2]\rangle - \mathrm{BraCKet}[\{\phi_3[1]\},h[1],\{\phi_3[1]\}]\langle\phi_1[3]\,|\phi_3[3]\rangle\langle\phi_2[2]\,|\phi_1[2]\rangle - \mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_3[3]\}]\langle\phi_1[1]\,|\phi_3[1]\rangle\langle\phi_2[2]\,|\phi_2[2]\rangle + \mathrm{BraCKet}[\{\phi_3[1]\},h[1],\{\phi_3[1]\}]\langle\phi_1[3]\,|\phi_3[3]\rangle\langle\phi_2[2]\,|\phi_2[2]\rangle + \mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_3[3]\}]\Big(-\langle\phi_1[1]\,|\phi_2[1]\rangle\langle\phi_2[2]\,|\phi_1[2]\rangle + \langle\phi_1[1]\,|\phi_1[1]\rangle\langle\phi_2[2]\,|\phi_2[2]\rangle\Big) - \mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_2[3]\}]\langle\phi_1[1]\,|\phi_1[1]\rangle\langle\phi_2[2]\,|\phi_3[2]\rangle + \mathrm{BraCKet}[\{\phi_3[3]\},h[3],\{\phi_3[3]\}]\langle\phi_1[1]\,|\phi_2[1]\rangle\langle\phi_2[2]\,|\phi_3[2]\rangle + \mathrm{BraCKet}[\{\phi_3[1]\},h[1],\{\phi_3[1]\}]\Big(\langle\phi_1[3]\,|\phi_3[3]\rangle\langle\phi_2[2]\,|\phi_2[2]\rangle - \langle\phi_1[3]\,|\phi_2[3]\rangle\langle\phi_2[2]\,|\phi_3[2]\rangle\Big) - \mathrm{BraCKet}[\{\phi_3[1]\},h[1],\{\phi_2[1]\}]\Big(\langle\phi_1[3]\,|\phi_3[3]\rangle\langle\phi_2[2]\,|\phi_2[2]\rangle - \langle\phi_1[3]\,|\phi_2[3]\rangle\langle\phi_2[2]\,|\phi_3[2]\rangle\Big) + \mathrm{BraCKet}[\{\phi_3[2]\},h[2],\{\phi_2[2]\}]\langle\phi_1[1]\,|\phi_3[1]\rangle\langle\phi_2[3]\,|\phi_1[3]\rangle -$$

$$\mathrm{BraCKet}[\{\phi_1[1]\},h[1],\{\phi_2[1]\}]\langle\phi_2[2]\,|\phi_1[2]\rangle + \mathrm{BraCKet}[\{\phi_1[1]\},h[1],\{\phi_1[1]\}]\Big(\langle\phi_2[2]\,|\phi_2[2]\rangle\Big)\langle\phi_3[3]\,|\phi_3[3]\rangle\Big)$$

$$\frac{1}{3}\Big(\langle\phi_1[1]\,|\,h[1]\,|\,\phi_1[1]\rangle + \langle\phi_1[2]\,|\,h[2]\,|\,\phi_1[2]\rangle + \langle\phi_1[3]\,|\,h[3]\,|\,\phi_1[3]\rangle + \langle\phi_2[1]\,|\,h[1]\,|\,\phi_2[1]\rangle + \langle\phi_2[2]\,|\,h[2]\,|\,\phi_2[2]\rangle + \langle\phi_2[3]\,|\,h[3]\,|\,\phi_2[3]\rangle + \langle\phi_3[1]\,|\,h[1]\,|\,\phi_3[1]\rangle + \langle\phi_3[2]\,|\,h[2]\,|\,\phi_3[2]\rangle + \langle\phi_3[3]\,|\,h[3]\,|\,\phi_3[3]\rangle\Big)$$

$$\langle\phi_1\,|\,h\,|\,\phi_1\rangle + \langle\phi_2\,|\,h\,|\,\phi_2\rangle + \langle\phi_3\,|\,h\,|\,\phi_3\rangle$$

The 1-electron contribution to expectation energy with Slater determinant is unsurprising

$$\langle E \rangle = \left\langle \Phi \middle| \sum_i \hat{h}_i \middle| \Phi \right\rangle + \left\langle \Phi \middle| \sum_{i<j} \hat{h}_{i,j} \middle| \Phi \right\rangle + V_{\mathrm{NN}}^{\mathrm{Coul}}$$

$$\hat{h}_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0} r_{i,A}$$

$$\left\langle \Phi \middle| \sum_i \hat{h}_i \middle| \Phi \right\rangle = \sum_i \left\langle \phi_i \middle| \hat{h} \middle| \phi_i \right\rangle \equiv \sum_i h_{i,i}$$

- Value tends to be negative due to electron-nucleus Coulomb contribution
- Can be positive for wavefunctions with many nodes
  - large KE

But the 2-electron contribution to expectation energy with Slater determinant *is* surprising

$$\langle E \rangle = \left\langle \Phi \middle| \sum_i \hat{h}_i \middle| \Phi \right\rangle + \left\langle \Phi \middle| \sum_{i<j} \hat{h}_{i,j} \middle| \Phi \right\rangle + V_{\mathrm{NN}}^{\mathrm{Coul}}$$

```
nM = 2;        2 orbitals
tauList = Range[nM]
BraCKet[{Φ[tauList]},
  Sum[1/r[i, j], {j, 2, nM}, {i, j - 1}],
  {Φ[tauList]}];
% //. sumRules // Simplify
% //. orthonormalRule // Simplify
% //. mullikenFormRule
```

$\hat{h}_{i,j}$

{1, 2} List of coordinates, τ

$$\left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[2]\,\phi_2[1] \right\rangle - \left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[1]\,\phi_2[2] \right\rangle$$

Raw form of <Φ|Σh|Φ>

$$\left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[2]\,\phi_2[1] \right\rangle - \left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[1]\,\phi_2[2] \right\rangle$$

After applying orthonormal rule (no change)

[11|22] - [12|21] Mulliken form

But the 2-electron contribution to expectation energy with Slater determinant *is* surprising

$$\langle E \rangle = \left\langle \Phi \middle| \sum_i \hat{h}_i \middle| \Phi \right\rangle + \left\langle \Phi \middle| \sum_{i<j} \hat{h}_{i,j} \middle| \Phi \right\rangle + V_{\mathrm{NN}}^{\mathrm{Coul}}$$

```
nM = 2;        2 orbitals
tauList = Range[nM]
BraCKet[{Φ[tauList]},
  Sum[1/r[i, j], {j, 2, nM}, {i, j - 1}],
  {Φ[tauList]}];
% //. sumRules // Simplify
% //. orthonormalRule // Simplify
% //. mullikenFormRule
```

$\hat{h}_{i,j}$

{1, 2} List of coordinates, τ

$$\left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[2]\,\phi_2[1] \right\rangle - \left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[1]\,\phi_2[2] \right\rangle$$

Raw form of <Φ|Σh|Φ>

$$\left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[2]\,\phi_2[1] \right\rangle - \left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[1]\,\phi_2[2] \right\rangle$$

After applying orthonormal rule (no change)

[11|22] - [12|21] Mulliken form

Note the difference in these two terms

$$\left\langle \phi_1[1]\,\phi_2[2] \middle| \frac{1}{r}[1,2] \middle| \phi_1[1]\,\phi_2[2] \right\rangle - \left\langle \phi_1[1]\,\phi_2[2] \middle| \frac{1}{r}[1,2] \middle| \phi_1[2]\,\phi_2[1] \right\rangle$$

[11|22]

[12]|21] Mulliken form

But the 2-electron contribution to expectation energy with Slater determinant *is* surprising

$$\langle E \rangle = \left\langle \Phi \middle| \sum_i \hat{h}_i \middle| \Phi \right\rangle + \left\langle \Phi \middle| \sum_{i<j} \hat{h}_{i,j} \middle| \Phi \right\rangle + V_{\mathrm{NN}}^{\mathrm{Coul}}$$

2 orbitals

```
nM = 2;
tauList = Range[nM]
BraCKet[{Φ[tauList]},
  Sum[1/r[i, j], {j, 2, nM}, {i, j - 1}],
  {Φ[tauList]}];
% //. sumRules // Simplify
% //. orthonormalRule // Simplify
% //. mullikenFormRule
```

$\hat{h}_{i,j}$

{1, 2} List of coordinates, τ

$$\left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[2]\,\phi_2[1] \right\rangle - \left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[1]\,\phi_2[2] \right\rangle$$

Raw form of <Φ|Σh|Φ>

$$\left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[2]\,\phi_2[1] \right\rangle - \left\langle \phi_1[2]\,\phi_2[1] \middle| \frac{1}{r}[1,2] \middle| \phi_1[1]\,\phi_2[2] \right\rangle$$

After applying orthonormal rule (no change)

[11|22] - [12|21] Mulliken form

3 orbitals

```
nM = 3;
tauList = Range[nM]
BraCKet[{Φ[tauList]}, Sum[1/r[i, j], {j, 2, nM}, {i, j - 1}], {Φ[tauList]}];
% //. sumRules // Simplify;
% //. orthonormalRule // Simplify
% //. mullikenFormRule
```

{1, 2, 3}

$$\left\langle \phi_1[3]\,\phi_2[1] \middle| \frac{1}{r}[1,3] \middle| \phi_1[3]\,\phi_2[1] \right\rangle - \left\langle \phi_1[3]\,\phi_2[1] \middle| \frac{1}{r}[1,3] \middle| \phi_1[1]\,\phi_2[3] \right\rangle + \left\langle \phi_1[3]\,\phi_3[1] \middle| \frac{1}{r}[1,3] \middle| \phi_1[3]\,\phi_3[1] \right\rangle -$$
$$\left\langle \phi_1[3]\,\phi_3[1] \middle| \frac{1}{r}[1,3] \middle| \phi_1[1]\,\phi_3[3] \right\rangle + \left\langle \phi_2[3]\,\phi_3[1] \middle| \frac{1}{r}[1,3] \middle| \phi_2[3]\,\phi_3[1] \right\rangle - \left\langle \phi_2[3]\,\phi_3[1] \middle| \frac{1}{r}[1,3] \middle| \phi_2[1]\,\phi_3[3] \right\rangle$$

[11|22] + [11|33] - [12|21] - [13|31] + [22|33] - [23|32]

Electron Repulsion Integrals (ERI): one has a simple physical interpretation, the other doesn't

- Coulomb integral is average Coulomb repulsion

$$\left\langle \phi_1[2]\,\phi_2[1] \left| \frac{1}{r}[1,2] \right| \phi_1[2]\,\phi_2[1] \right\rangle \qquad [11|22] = \int \underbrace{\varphi_1^*(\tau_1)\varphi_1(\tau_1)}_{p(\tau_1)} \underbrace{\varphi_2^*(\tau_2)\varphi_2(\tau_2)}_{p(\tau_2)} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_1 d\tau_2$$

spin-orbitals (not just spatial), but Mma doesn't typeset φ

- There's no similar interpretation for exchange

$$\left\langle \phi_1[2]\,\phi_2[1] \left| \frac{1}{r}[1,2] \right| \phi_1[1]\,\phi_2[2] \right\rangle \qquad [12|21] = \int \underbrace{\varphi_1^*(\tau_1)\varphi_2(\tau_1)}_{?} \underbrace{\varphi_2^*(\tau_2)\varphi_1(\tau_2)}_{?} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_1 d\tau_2$$

  - Typically positive, and smaller in magnitude than Coulomb integral
  - Cancels Coulomb integral when $i = j$

Energy expectation is sum of 1-electron contributions and Coulomb and exchange ERIs

- Putting it all together

Sums are over orbital basis functions

$$\langle E \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{i,j} ([ii|jj] - [ij|ji]) + V_{\mathrm{NN}}^{\mathrm{Coul}}$$

1-electron integral:
KE + electron-nuclear
Coulomb attraction

2-electron integral:
Coulomb repulsion

2-electron integral:
Coulomb exchange

- This is specifically for a wavefunction given as a Slater determinant

Suggested Reading/Viewing

- Autschbach Ch. 1, Secs. 7.7, 8.1