

```
In[ ]:= SetDirectory[NotebookDirectory[]];
Import["init.wl"];
```

Exact Hubbard model solution for Li₂ molecule using (2 s)² orbital basis.

$$\text{In[]:= } \mathbf{H} = \begin{pmatrix} 2e & 0 & V & V & 0 & 0 \\ 0 & 2e & V & V & 0 & 0 \\ V & V & 2e+U & 0 & 0 & 0 \\ V & V & 0 & 2e+U & 0 & 0 \\ 0 & 0 & 0 & 0 & 2e & 0 \\ 0 & 0 & 0 & 0 & 0 & 2e \end{pmatrix};$$

```
In[ ]:= ϕ1 = {1, 0, 0, 0, 0, 0};
ϕ2 = {0, 1, 0, 0, 0, 0};
ϕ3 = {0, 0, 1, 0, 0, 0};
ϕ4 = {0, 0, 0, 1, 0, 0};
ϕ5 = {0, 0, 0, 0, 1, 0};
ϕ6 = {0, 0, 0, 0, 0, 1};
```

$$\phi a = (\phi 1 + \phi 2) / \sqrt{2};$$

$$\phi b = (\phi 3 + \phi 4) / \sqrt{2};$$

$$\phi c = (\phi 1 - \phi 2) / \sqrt{2};$$

$$\phi d = (\phi 3 - \phi 4) / \sqrt{2};$$

$$\psi[\eta_] := \frac{1}{\sqrt{2}} (2 \sin[\eta] \cos[\eta] \phi b + \phi a) // \text{Simplify}$$

```
In[ ]:= hs = {{ϕa.H.ϕa, ϕa.H.ϕb}, {ϕb.H.ϕa, ϕb.H.ϕb}};
Eigenvalues[hs]
```

$$\text{Out[]:= } \left\{ \frac{1}{2} (4e + U - \sqrt{U^2 + 16V^2}), \frac{1}{2} (4e + U + \sqrt{U^2 + 16V^2}) \right\}$$

```
In[ ]:= Eigenvectors[hs]
```

$$\text{Out[]:= } \left\{ \left\{ -\frac{U + \sqrt{U^2 + 16V^2}}{4V}, 1 \right\}, \left\{ -\frac{U - \sqrt{U^2 + 16V^2}}{4V}, 1 \right\} \right\}$$

```
In[ ]:=
```

```
ha = {{ϕc.H.ϕc, ϕc.H.ϕd}, {ϕd.H.ϕc, ϕd.H.ϕd}};
Eigenvalues[hs]
```

$$\text{Out[]:= } \left\{ \frac{1}{2} (4e + U - \sqrt{U^2 + 16V^2}), \frac{1}{2} (4e + U + \sqrt{U^2 + 16V^2}) \right\}$$

```
In[ ]:= Eigenvalues[ha]
```

$$\text{Out[]:= } \{2e, 2e + U\}$$

```
In[*]:= huhf =  $\psi[\eta].H.\psi[\eta]$  // Simplify
```

```
huhf /. {e  $\rightarrow$  0, V  $\rightarrow$  -1} /.  $\eta \rightarrow \pi/4$ 
```

```
Out[*]:=  $e + 4 V \cos[\eta] \sin[\eta] + 2 (2 e + U) \cos[\eta]^2 \sin[\eta]^2$ 
```

```
Out[*]:=  $-2 + \frac{U}{2}$ 
```

```
In[*]:=  $\left\{ \frac{1}{2} (4 e + U - \sqrt{U^2 + 16 V^2}), \frac{1}{2} (4 e + U + \sqrt{U^2 + 16 V^2}) \right\}$  // TeXForm
```

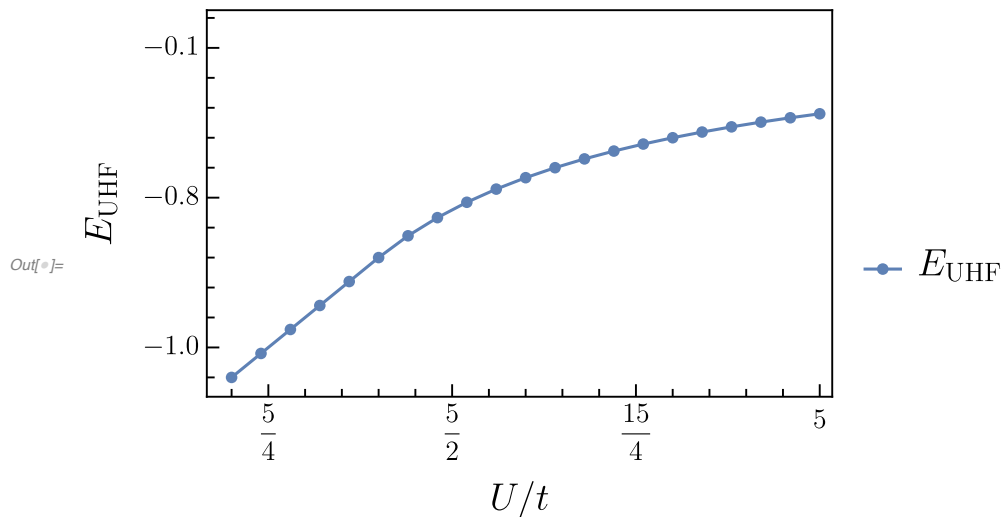
```
Out[*]//TeXForm=
```

```
 $\left\{ \frac{1}{2} \left( 4 e - \sqrt{U^2 + 16 V^2} + U \right), \frac{1}{2} \left( 4 e + \sqrt{U^2 + 16 V^2} + U \right) \right\}$ 
```

```
In[*]:= huhf =  $2 (e + (2 e + U) \cos[\eta]^2 \sin[\eta]^2 + V \sin[2 \eta])$ 
```

```
Out[*]:=  $2 (e + (2 e + U) \cos[\eta]^2 \sin[\eta]^2 + V \sin[2 \eta])$ 
```

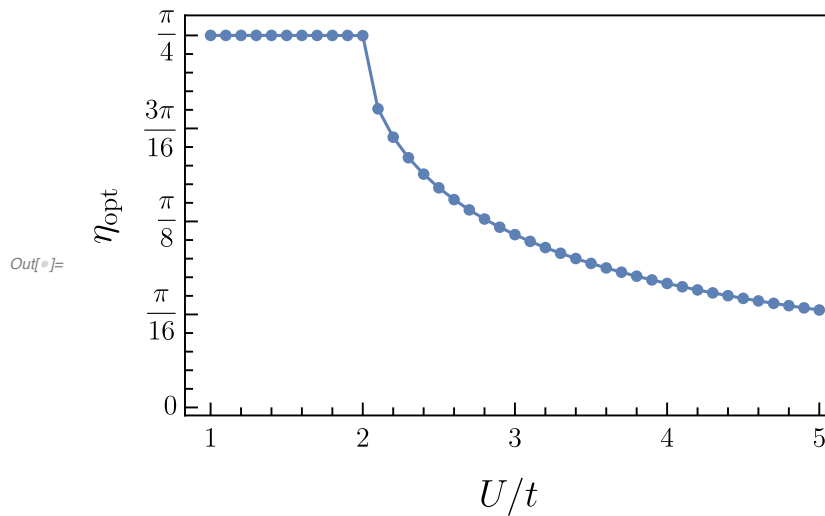
```
In[*]:= uhf = ListPlot[
  Table[{U, FindMinimum[huhf /. {e  $\rightarrow$  0.0, V  $\rightarrow$  -1.0}, { $\eta$ , 0.2  $\pi$ }, AccuracyGoal  $\rightarrow$  4,
    PrecisionGoal  $\rightarrow$  4][[1]]}, {U, 1, 5, 0.2}],
  Joined  $\rightarrow$  {True, True}, PlotMarkers  $\rightarrow$  {Automatic},
  PlotLegends  $\rightarrow$  {tex["E_\\text{UHF}"], 20}},
  FrameLabel  $\rightarrow$  {tex["U/t", 20], tex["E_\\text{UHF}"], 20}},
  FrameTicks  $\rightarrow$  {{tf[-2.0, 0.5, 4, 5, 10.5 * 100 / 72, 10], None},
    {tf[0, 5, 4, 5, 10.5 * 100 / 72, 10], None}},
  Frame  $\rightarrow$  True,
  ImageSize  $\rightarrow$  10 * 100 / 2.54,
  FrameStyle  $\rightarrow$  Directive[Black, AbsoluteThickness[1]]
]
```



```

In[ ]:= mix = ListPlot[
  Table[{U,  $\eta$  /. FindMinimum[huhf /. {e  $\rightarrow$  0, V  $\rightarrow$  -1}, { $\eta$ , 0.2  $\pi$ }, AccuracyGoal  $\rightarrow$  4,
    PrecisionGoal  $\rightarrow$  4][[2]]}, {U, 1, 5, 0.1}],
  Joined  $\rightarrow$  {True, True}, PlotMarkers  $\rightarrow$  {Automatic},
  FrameLabel  $\rightarrow$  {tex["U/t", 20], tex["\\eta_\\text{opt}", 20]},
  FrameTicks  $\rightarrow$  {{tf[0,  $\frac{\pi}{4}$ , 4, 5, 10.5 * 100 / 72, 10], None},
    {tf[1, 5, 4, 5, 10.5 * 100 / 72, 10], None}},
  Frame  $\rightarrow$  True,
  ImageSize  $\rightarrow$  10 * 100 / 2.54,
  FrameStyle  $\rightarrow$  Directive[Black, AbsoluteThickness[1]]]

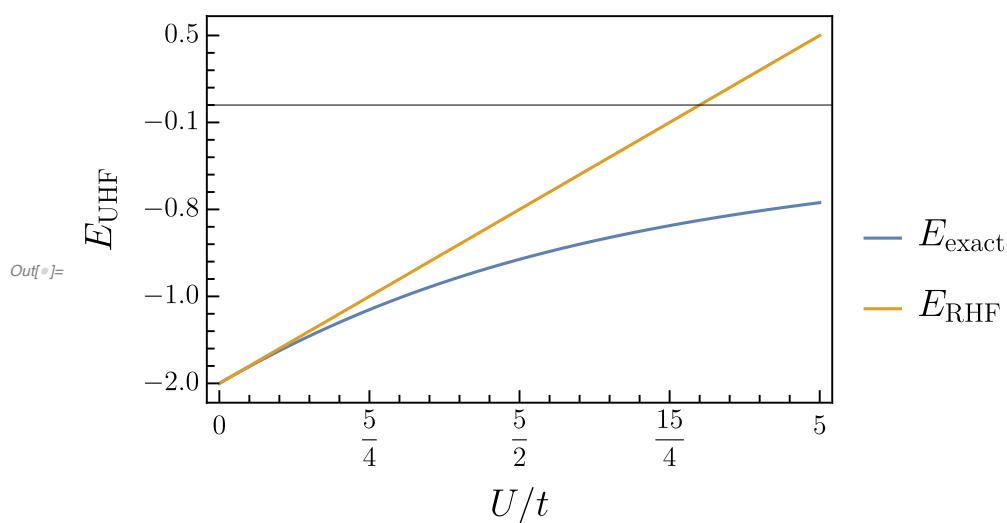
```



```

In[ ]:= em = 2 e + U/2 -  $\sqrt{(U/2)^2 + 4 V^2}$  /. {e -> 0, V -> -1};
rhf = U/2 - 2;
p2 = Plot[{em, rhf}, {U, 0, 5},
  PlotLegends -> {tex["E_\\text{exact}"], 20], tex["E_\\text{RHF}"], 20]],
  FrameLabel -> {tex["U/t", 20], tex["E_\\text{UHF}"], 20]],
  FrameTicks -> {{tf[-2, 0.5, 4, 5, 10.5 * 100/72, 10], None},
    {tf[0, 5, 4, 5, 10.5 * 100/72, 10], None}},
  Frame -> True,
  ImageSize -> 10 * 100/2.54,
  FrameStyle -> Directive[Black, AbsoluteThickness[1]]]

```



```

In[ ]:= var = Show[p2, uhf,
  Epilog -> {Line[{{2, 1}, {2, -1}}],
    Style[Text[tex["\\text{Delocalized}"], 14], {1.0, 0.25}], 14],
    Style[Text[tex["\\text{Localized}"], 14], {2.8, 0.25}], 14]
}]

```

