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

Exact Hubbard model solution for Li_2 molecule using $(2\,s)^2$ orbital basis.

In[•]:=

$$H = \begin{pmatrix} 2e & 0 & V & V & 0 & 0 \\ 0 & 2e & V & V & 0 & 0 \\ V & V & 2e+U & 0 & 0 & 0 \\ V & V & 0 & 2e+U & 0 & 0 \\ 0 & 0 & 0 & 0 & 2e & 0 \\ 0 & 0 & 0 & 0 & 0 & 2e \end{pmatrix};$$

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};
```

$$\phi a = (\phi 1 + \phi 2) \Big/ \sqrt{2};$$
$$\phi b = (\phi 3 + \phi 4) \Big/ \sqrt{2};$$

$$\phi c = (\phi 1 - \phi 2) \Big/ \sqrt{2};$$
$$\phi d = (\phi 3 - \phi 4) \Big/ \sqrt{2};$$

$$\psi[\eta\_] := \frac{1}{\sqrt{2}} \left(2\,\mathrm{Sin}[\eta]\,\mathrm{Cos}[\eta]\,\phi b + \phi a\right) \mathbin{//} \mathrm{Simplify}$$

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

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

In[•]:=
```
Eigenvectors[hs]
```

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

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

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

In[•]:=
```
Eigenvalues[ha]
```

Out[•]=
$$\{2\,e, 2\,e + U\}$$

In[∘]:=
```
huhf = ψ[η].H.ψ[η] // Simplify
huhf /. {e → 0, V → -1} /. η → π / 4
```

Out[∘]= $e + 4 V \text{Cos}[\eta] \text{Sin}[\eta] + 2 (2 e + U) \text{Cos}[\eta]^2 \text{Sin}[\eta]^2$

Out[∘]= $-2 + \frac{U}{2}$

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

Out[∘]//TeXForm=

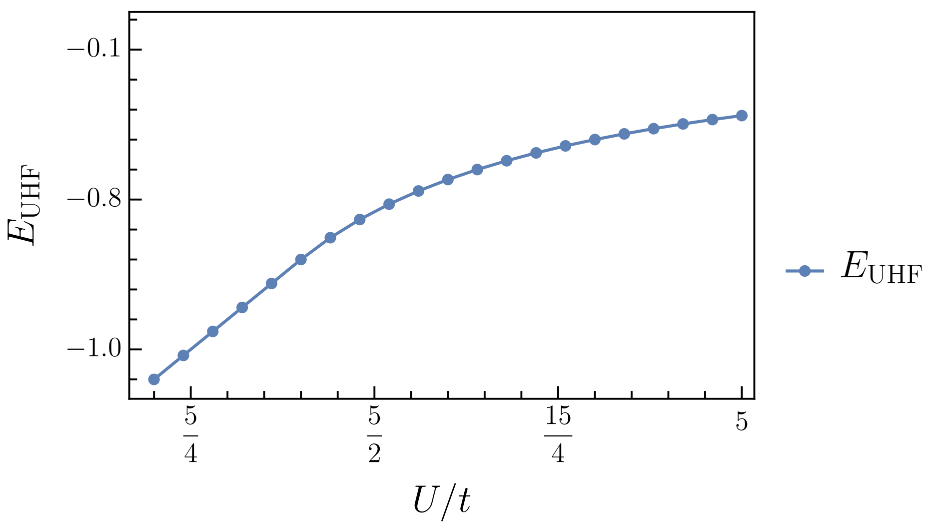
```
\left\{\frac{1}{2} \left(4 e-\sqrt{U^2+16 V^2}+U\right),\frac{1}{2} \left(4
   e+\sqrt{U^2+16 V^2}+U\right)\right\}
```

In[∘]:= huhf = $2 \left(e + (2 e + U) \text{Cos}[\eta]^2 \text{Sin}[\eta]^2 + V \text{Sin}[2 \eta]\right)$

Out[∘]= $2 \left(e + (2 e + U) \text{Cos}[\eta]^2 \text{Sin}[\eta]^2 + V \text{Sin}[2 \eta]\right)$

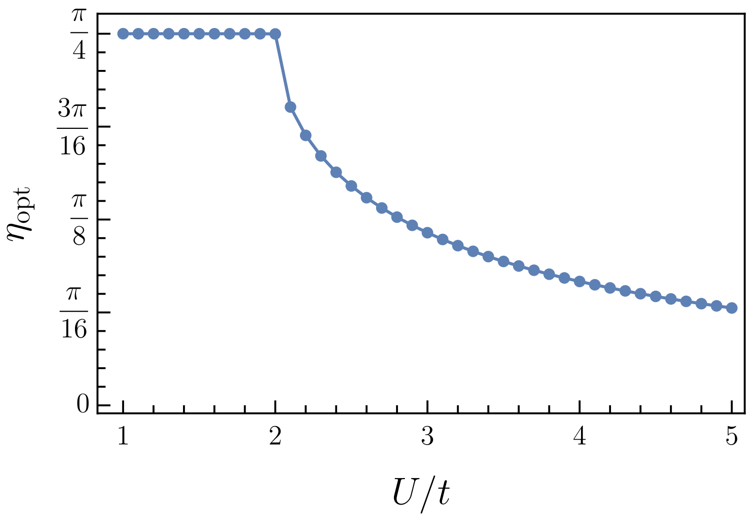
In[∘]:=
```
uhf = ListPlot[
  Table[{U, FindMinimum[huhf /. {e → 0.0, V → -1.0}, {η, 0.2 π}, AccuracyGoal → 4,
      PrecisionGoal → 4][[1]]}, {U, 1, 5, 0.2}],
  Joined → {True, True}, PlotMarkers → {Automatic},
  PlotLegends -> {tex["E_\\text{UHF}", 20]},
  FrameLabel → {tex["U/t", 20], tex["E_\\text{UHF}", 20]},
  FrameTicks → {{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 → True,
  ImageSize → 10 * 100 / 2.54,
  FrameStyle → Directive[Black, AbsoluteThickness[1]]
 ]
```

Out[∘]=



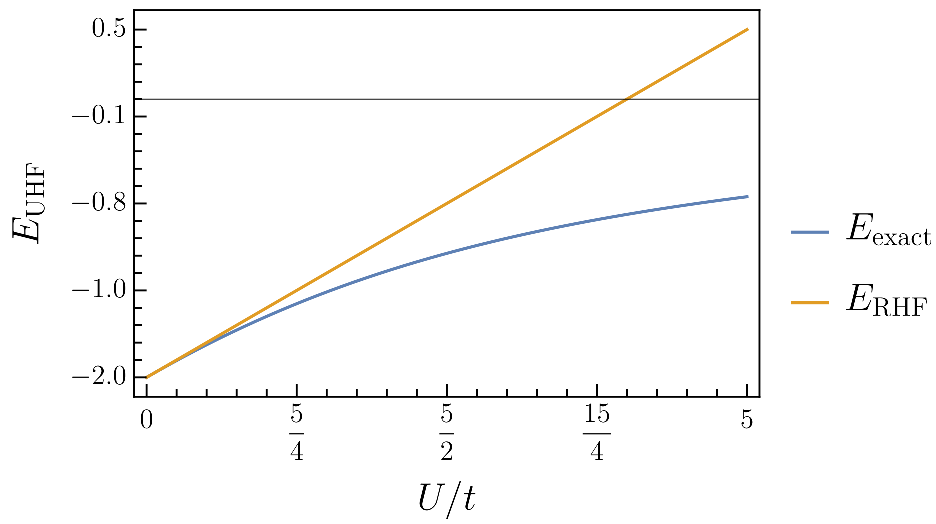
In[•]:=
```
mix = ListPlot[
  Table[{U, η /. FindMinimum[huhf /. {e → 0, V → -1}, {η, 0.2 π}, AccuracyGoal → 4,
       PrecisionGoal → 4][[2]]}, {U, 1, 5, 0.1}],
  Joined → {True, True}, PlotMarkers → {Automatic},
  FrameLabel → {tex["U/t", 20], tex["\\eta_\\text{opt}", 20]},
  FrameTicks → {{tf[0, π/4,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

Out[•]=



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]]]
```

Out[•]=



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]
  }]
```

Out[•]=