In[•]:=
```
SetOptions[SelectedNotebook[],
 PrintingStyleEnvironment → "Printout", ShowSyntaxStyles → True]
```

In[•]:=
```
<< Notation`
```

In[•]:=
```
(* Simplify the notation for the
 formulas: index vectors based on a subscript notation *)
Notation[ x_n_ ⟺ x_[[n_]] ]
```

In[•]:=
```
d = 1.0; (* Equilibrium bond length *)
α = Reverse@{13.00773, 1.962079, 0.444529, 0.1219492} & /@ Range[1, 2] // Flatten
```

Out[•]=
```
{0.121949, 0.444529, 1.96208, 13.0077, 0.121949, 0.444529, 1.96208, 13.0077}
```

In[•]:=
```
atomsPts = {{0, 0, 0}, {d, 0, 0}}; (* Atomic positions *)
Z = Partition[Table[#, {n, 1, 4}] & /@ atomsPts // Flatten, 3]
 (* Array of positions for the coefficients α *)
```

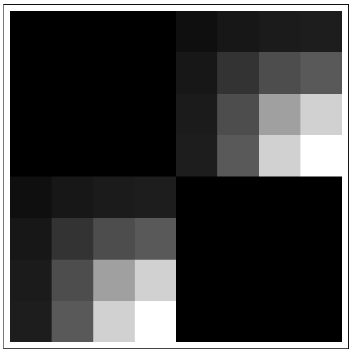
Out[•]=
```
{{0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0},
 {1., 0, 0}, {1., 0, 0}, {1., 0, 0}, {1., 0, 0}}
```

In[•]:=

$$K = \text{Array}\left[\text{Exp}\left[-\frac{\alpha_{\#1}\,\alpha_{\#2}}{\alpha_{\#1}+\alpha_{\#2}}\,\text{Norm}[Z_{\#1}-Z_{\#2}]^2\right]\&,\ \{8,8\}\right];\ (*\ \text{Coefficients matrix } K_{p,q}\ *)$$

```
#[K] & /@ {SymmetricMatrixQ, ArrayPlot, MatrixForm}
```

Out[•]=

{True, ,

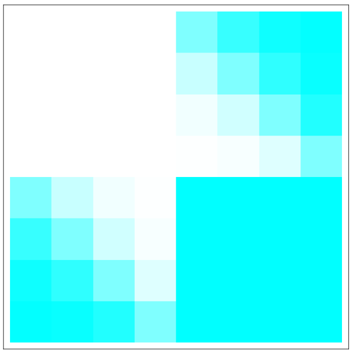
$$\begin{pmatrix}
1. & 1. & 1. & 1. & 0.940847 \\
1. & 1. & 1. & 1. & 0.90874 \\
1. & 1. & 1. & 1. & 0.891533 \\
1. & 1. & 1. & 1. & 0.886197 \\
0.940847 & 0.90874 & 0.891533 & 0.886197 & 1. \\
0.90874 & 0.800704 & 0.695991 & 0.650613 & 1. \\
0.891533 & 0.695991 & 0.374921 & 0.181789 & 1. \\
0.886197 & 0.650613 & 0.181789 & 0.00149764 & 1.
\end{pmatrix}$$

In[•]:=

$$R = \text{Array}\left[\frac{\alpha_{\#1}\,Z_{\#1}+\alpha_{\#2}\,Z_{\#2}}{\alpha_{\#1}+\alpha_{\#2}}\ \&,\ \{8,8\}\right];\ (*\ \text{Distances matrix } R_{p,q}\ *)$$

```
#[R] & /@ {SymmetricMatrixQ, ArrayPlot, MatrixForm}
```

Out[ ]=

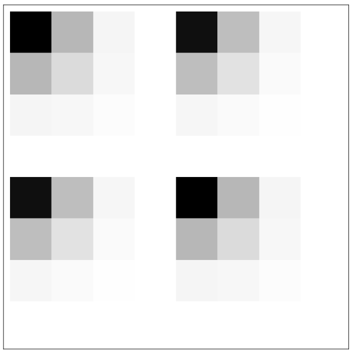
$\{$False, ,

$$\begin{pmatrix}
\begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix}\\
\begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix}\\
\begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix}\\
\begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.\\0.\\0.\end{pmatrix}\\
\begin{pmatrix}0.5\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.215276\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.0585161\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.0092886\\0.\\0.\end{pmatrix}\\
\begin{pmatrix}0.784724\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.5\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.184712\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.033044\\0.\\0.\end{pmatrix}\\
\begin{pmatrix}0.941484\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.815288\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.5\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.131069\\0.\\0.\end{pmatrix}\\
\begin{pmatrix}0.990712\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.966955\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.868931\\0.\\0.\end{pmatrix} & \begin{pmatrix}0.5\\0.\\0.\end{pmatrix}
\end{pmatrix}$$

In[ ]:= $S = \text{Array}\left[\left(\frac{\pi}{\alpha_{\#1} + \alpha_{\#2}}\right)^{3/2} K_{\#1,\#2}\ \&,\ \{8, 8\}\right];$ (* Overlap matrix $S_{p,q}$ *)

```
#[S] & /@ {SymmetricMatrixQ, ArrayPlot, MatrixForm}
```

Out[ ]=

$\{$True, ,

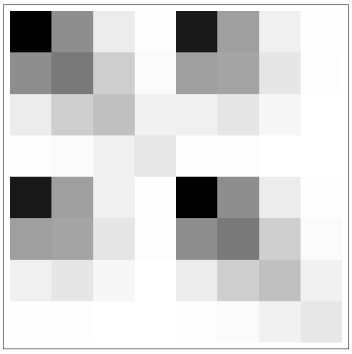
$$\begin{pmatrix}
46.2287 & 13.0602 & 1.85084 & 0.117043 & 43.494\\
13.0602 & 6.64247 & 1.49148 & 0.112858 & 11.868\\
1.85084 & 1.49148 & 0.716317 & 0.0961392 & 1.6500\\
0.117043 & 0.112858 & 0.0961392 & 0.0419641 & 0.1037\\
43.4941 & 11.8683 & 1.65009 & 0.103723 & 46.228\\
11.8683 & 5.31865 & 1.03805 & 0.0734269 & 13.060\\
1.65009 & 1.03805 & 0.268562 & 0.017477 & 1.8508\\
0.103723 & 0.0734269 & 0.017477 & 0.000062847 & 0.1170
\end{pmatrix}$$

In[ ]:= $T = \text{Array}\left[\frac{\alpha_{\#1}\,\alpha_{\#2}}{\alpha_{\#1} + \alpha_{\#2}}\left(3 - 2\,\frac{\alpha_{\#1}\,\alpha_{\#2}}{\alpha_{\#1} + \alpha_{\#2}}\,\text{Norm}[Z_{\#1} - Z_{\#2}]^2\right) S_{\#1,\#2}\ \&,\ \{8, 8\}\right];$

(* Kinetic energy matrix $T_{p,q}$ *)

```
#[T] & /@ {SymmetricMatrixQ, ArrayPlot, MatrixForm}
```

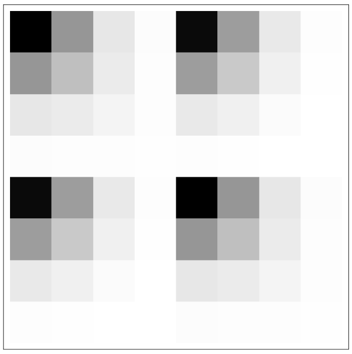
Out[ ]=

{True, ,
$$\begin{pmatrix}
8.45632 & 3.74945 & 0.637503 & 0.042422 & 7.6 \\
3.74945 & 4.42916 & 1.62162 & 0.145532 & 3. \\
0.637503 & 1.62162 & 2.1082 & 0.491726 & 0.5 \\
0.042422 & 0.145532 & 0.491726 & 0.818786 & 0.03 \\
7.63269 & 3.1899 & 0.524852 & 0.0345662 & 8.4 \\
3.1899 & 3.02094 & 0.85594 & 0.0675523 & 3.7 \\
0.524852 & 0.85594 & 0.273461 & -0.0122114 & 0.6 \\
0.0345662 & 0.0675523 & -0.0122114 & -0.00409065 & 0.0
\end{pmatrix}$$

In[ ]:=

```
V = Total@Table[Array[If[Norm[R[#1,#2] - U] == 0, -(2 π)/(α[#1] + α[#2]) K[#1,#2],
    -S[#1,#2] 1/Norm[R[#1,#2] - U] Erf[Sqrt[α[#1] + α[#2]] Norm[R[#1,#2] - U]]] &, {8, 8}],
   {U, atomsPts}]; (* Potential energy matrix V_{p,q} *)
#[V] & /@ {SymmetricMatrixQ, ArrayPlot, MatrixForm}
```

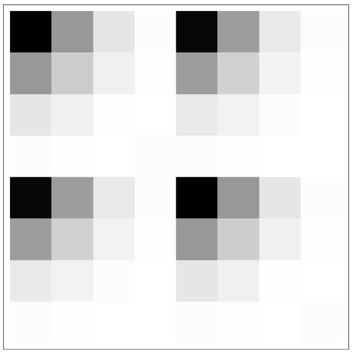
Out[ ]=

{True, ,
$$\begin{pmatrix}
-49.5733 & -20.4017 & -4.78952 & -0.595591 & -47 \\
-20.4017 & -12.4983 & -4.06016 & -0.579931 & -19 \\
-4.78952 & -4.06016 & -2.31383 & -0.515863 & -4. \\
-0.595591 & -0.579931 & -0.515863 & -0.283481 & -0. \\
-47.5078 & -19.0125 & -4.33849 & -0.528623 & -49 \\
-19.0125 & -10.5321 & -2.948 & -0.378339 & -20 \\
-4.33849 & -2.948 & -0.900982 & -0.0903486 & -4. \\
-0.528623 & -0.378339 & -0.0903486 & -0.00025131 & -0.
\end{pmatrix}$$

In[ ]:=

```
H = T + V;
#[H] & /@ {SymmetricMatrixQ, ArrayPlot, MatrixForm}
```

Out[ ]=

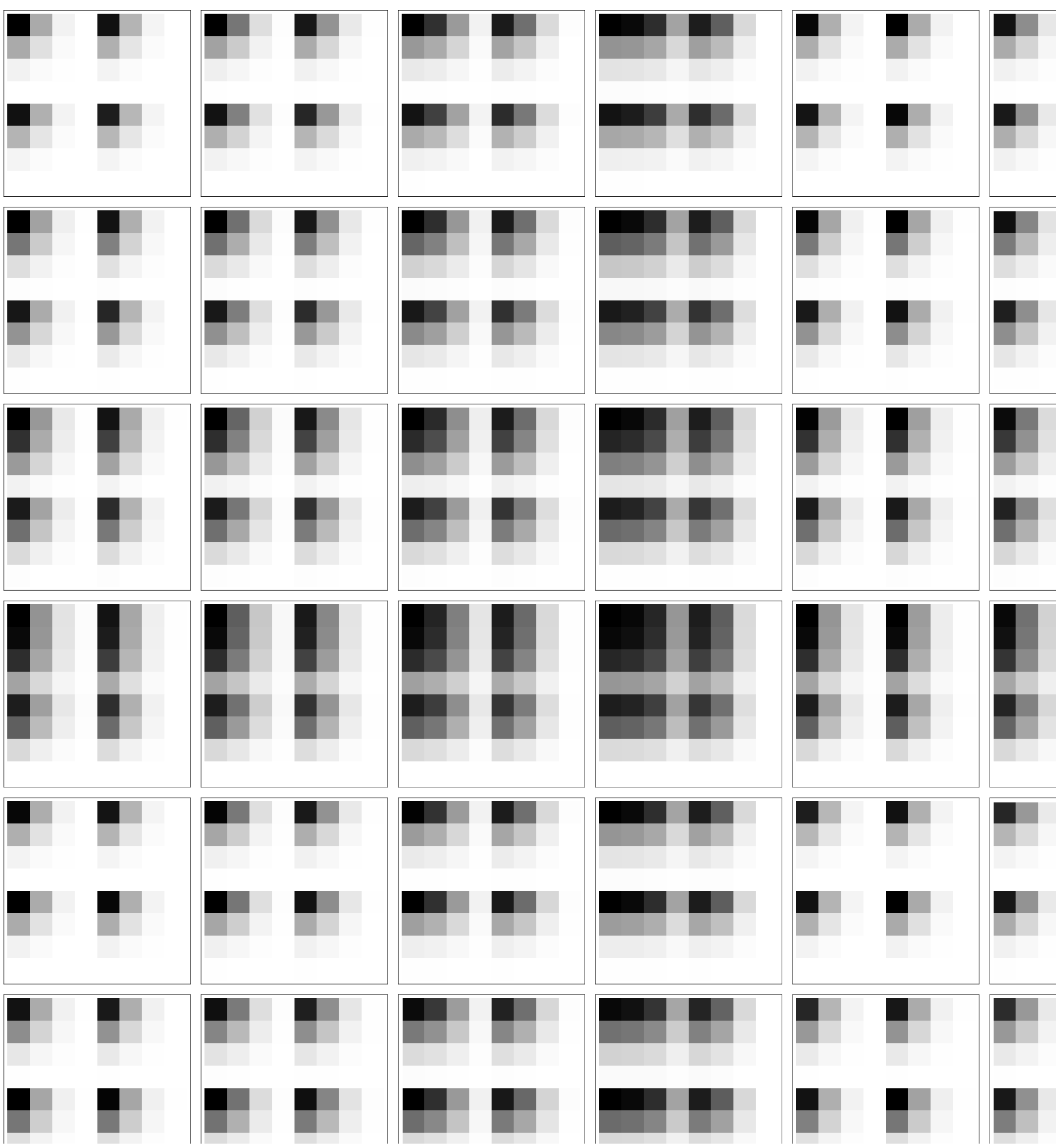
{True, ,
$$\begin{pmatrix}
-41.117 & -16.6522 & -4.15202 & -0.553169 & -39 \\
-16.6522 & -8.06909 & -2.43854 & -0.434398 & -15 \\
-4.15202 & -2.43854 & -0.205623 & -0.0241367 & -3. \\
-0.553169 & -0.434398 & -0.0241367 & 0.535304 & -0. \\
-39.8751 & -15.8226 & -3.81364 & -0.494057 & -4 \\
-15.8226 & -7.51116 & -2.09206 & -0.310786 & -16 \\
-3.81364 & -2.09206 & -0.627521 & -0.10256 & -4. \\
-0.494057 & -0.310786 & -0.10256 & -0.00434196 & -0.
\end{pmatrix}$$

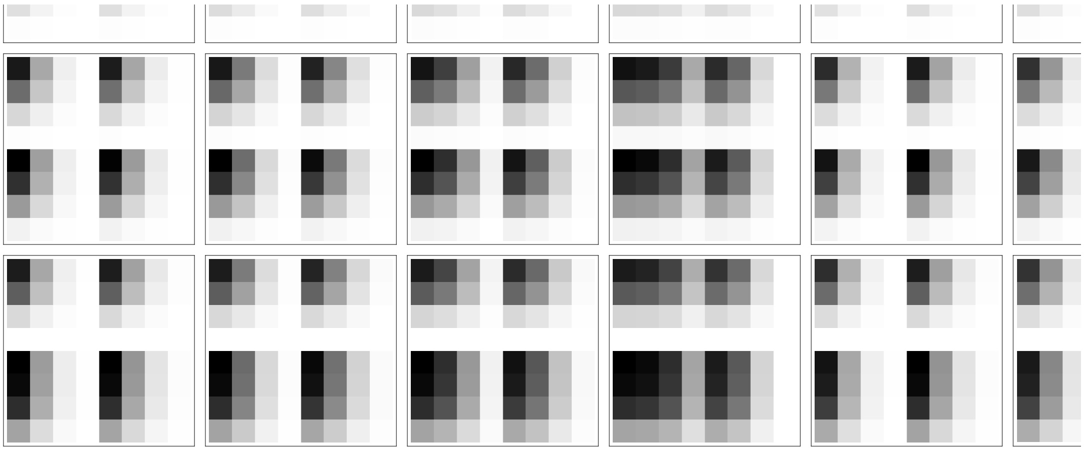
In[∘]:=

```
Q = Array[S_{#1,#3} S_{#2,#4} If[Norm[R_{#1,#3} - R_{#2,#4}] == 0, 2/Sqrt[π] Sqrt[((α_{#1} + α_{#3}) (α_{#2} + α_{#4}))/(α_{#1} + α_{#3} + α_{#2} + α_{#4})],
      1/Norm[R_{#1,#3} - R_{#2,#4}] Erf[Sqrt[((α_{#1} + α_{#3}) (α_{#2} + α_{#4}))/(α_{#1} + α_{#3} + α_{#2} + α_{#4})] Norm[R_{#1,#3} - R_{#2,#4}]]] &,
    {8, 8, 8, 8}]; (* Q_{p,r,q,s} matrix, it's an 8 by 8
  matrix containing 8 by 8 matrices *)
{SymmetricMatrixQ[Q],
 Grid@Array[ArrayPlot[Q_{#1,#2}, ImageSize → Tiny] &, {8, 8}], MatrixForm@Q}
```

Out[∘]=

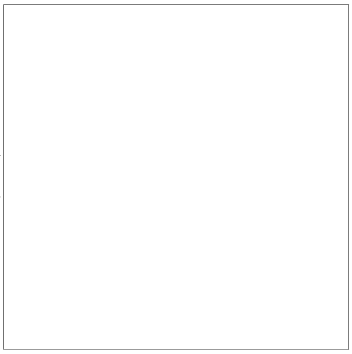
{False,





In[∘]:=
```
P = ConstantArray[0., {8, 8}];
#[P] & /@ {ArrayPlot, MatrixForm}
```

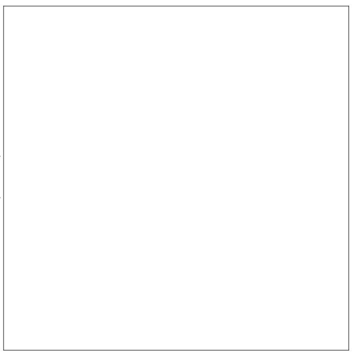
Out[∘]=

{  , $\begin{pmatrix} 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \end{pmatrix}$ }

In[∘]:= $G = \text{Array}\left[\sum_{r=1}^{8}\sum_{s=1}^{8} P_{r,s}\,(2\,Q_{\#1,r,\#2,s} - Q_{\#1,r,s,\#2})\ \&,\ \{8,\ 8\}\right]$ (* $G_{p,q}$ matrix *);

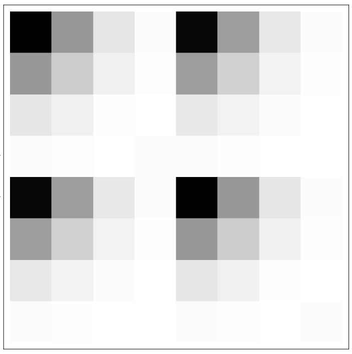
```
#[G] & /@ {ArrayPlot, MatrixForm}
```

Out[∘]=

{  , $\begin{pmatrix} 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\ 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \end{pmatrix}$ }

In[∘]:=
```
F = H + 1/2 G;
#[F] & /@ {ArrayPlot, MatrixForm}
```

Out[∘]=

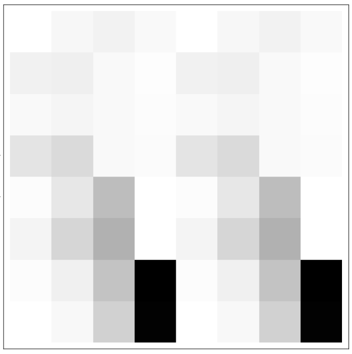
{  ,

-41.117	-16.6522	-4.15202	-0.553169	-39.8751
-16.6522	-8.06909	-2.43854	-0.434398	-15.8226
-4.15202	-2.43854	-0.205623	-0.0241367	-3.81364
-0.553169	-0.434398	-0.0241367	0.535304	-0.494057
-39.8751	-15.8226	-3.81364	-0.494057	-41.117
-15.8226	-7.51116	-2.09206	-0.310786	-16.6522
-3.81364	-2.09206	-0.627521	-0.10256	-4.15202
-0.494057	-0.310786	-0.10256	-0.00434196	-0.553169

In[∘]:=
```
matNorm[v_, M_] := v/Sqrt[v.M.v];
```

In[∘]:=
```
(* Doing the first eigensystem calculation as a testing ground *)
{evals, evecs} = Eigensystem[{F, S}];
(* Calculate the eigenvalues and eigenvectors *)
{evals, evecs} = {evals[[#]], evecs[[#]]} &@Ordering[evals];
(* Sort them in ascending order *)
evecs = matNorm[#, S] & /@ evecs;
(* Normalize them w.r.t. the overlap matrix S *)
If[AllTrue[Thread[#.S.# ≠ 1] & /@ evecs, TrueQ], Abort[], Nothing];
(* Perform a numerical divergence check *)
#[evecs] & /@ {ArrayPlot, MatrixForm}
```

Out[∘]=

{  ,

-0.0053109	-0.138633	-0.227877	-0.103876	-0.0053109
-0.247679	-0.290428	-0.112811	-0.0503944	0.247679
0.108453	-0.18563	-0.114518	-0.0553259	0.108453
-0.480872	0.64799	0.112376	0.07753	0.480872
-0.0670001	0.421322	-1.13493	0.00410123	-0.0670001
0.195647	-0.715908	1.35432	0.0142581	-0.195647
0.0648705	-0.272204	1.03771	-4.39883	-0.0648705
-0.0163136	0.129456	-0.793669	4.35218	-0.0163136

In[∘]:=
```
ϵ = 10^-6 // N; (* Accuracy level *)
```

In[∘]:=
```
(* Reset before the while-loop to assert correctness *)
evals = ConstantArray[0., {8}];
newEvals = evals + ϵ;
```

In[∘]:=
```
normDiffList = {}; (* List of the norm of the differences *)
```

In[∘]:=
```
(* While the new and previous eigenvalues are still different enough... *)
While[Norm[newEvals - evals] > ϵ,
  AppendTo[normDiffList, Norm[newEvals - evals]];
  (* Append the norm of the difference to the normDiffList list *)
  newEvals = evals; (* Overwrite the previous eigenvalues *)
  G = Array[Sum[Sum[P[r,s] (2 Q[#1,r,#2,s] - Q[#1,r,s,#2]), {s, 1, 8}], {r, 1, 8}] &, {8, 8}] (* Gp,q matrix *);
  F = H + 1/2 G; (* Compute the Fock operator from the G matrix *)
  {evals, evecs} = Eigensystem[{F, S}];
  (* Calculate the eigenvalues and eigenvectors *)
  {evals, evecs} = {evals[[#]], evecs[[#]]} &@Ordering[evals];
  (* Sort them in ascending order *)
  evecs = matNorm[#, S] & /@ evecs;
  (* Normalize them w.r.t. the overlap matrix S *)
  If[AllTrue[Thread[#.S.# ≠ 1] & /@ evecs, TrueQ], Abort[], Nothing];
  (* Perform a numerical divergence check *)
  (* Calculate the density matrix from the
   eigenvector evecs1 associated with the minimal eigenvalue *)
  P = 2 TensorProduct[evecs1, evecs1];
 ] // AbsoluteTiming // First
```

$$G = \mathrm{Array}\left[\sum_{r=1}^{8}\sum_{s=1}^{8} P_{r,s}\,(2\,Q_{\#1,r,\#2,s} - Q_{\#1,r,s,\#2})\ \&,\ \{8, 8\}\right]\ (*\ G_{p,q}\ \text{matrix}\ *);$$

Out[∘]=

```
0.05739
```

In[∘]:=
```
(* Return the first eigenvalue and the equilibrium bonding energy,
where 1/d is the Enucl term *)
Quantity[#, "HartreeEnergy"] & /@ {evals1, Total[P (H + 1/4 G), 2] + 1/d}
UnitConvert[#, "Electronvolts"] & /@ %
```

$$\text{Quantity}[\#, \text{"HartreeEnergy"}]\ \&\ /@\ \left\{evals_1,\ \text{Total}\left[P\left(H + \frac{1}{4} G\right), 2\right] + \frac{1}{d}\right\}$$

Out[∘]=

$\{-0.669956\ E_h,\ -1.07855\ E_h\}$

Out[∘]=

$\{-18.2304\ \text{eV},\ -29.3488\ \text{eV}\}$

In[∘]:=
```
ListStepPlot[Drop[normDiffList, 1], PlotRange → Full]
(* Measurements give 0.05 seconds for the convergence time for an SCF loop *)
```

Out[ ]=