Potential Energy Surface and Transition State Theory

The London-Eyring-Polanyi-Sato Potential

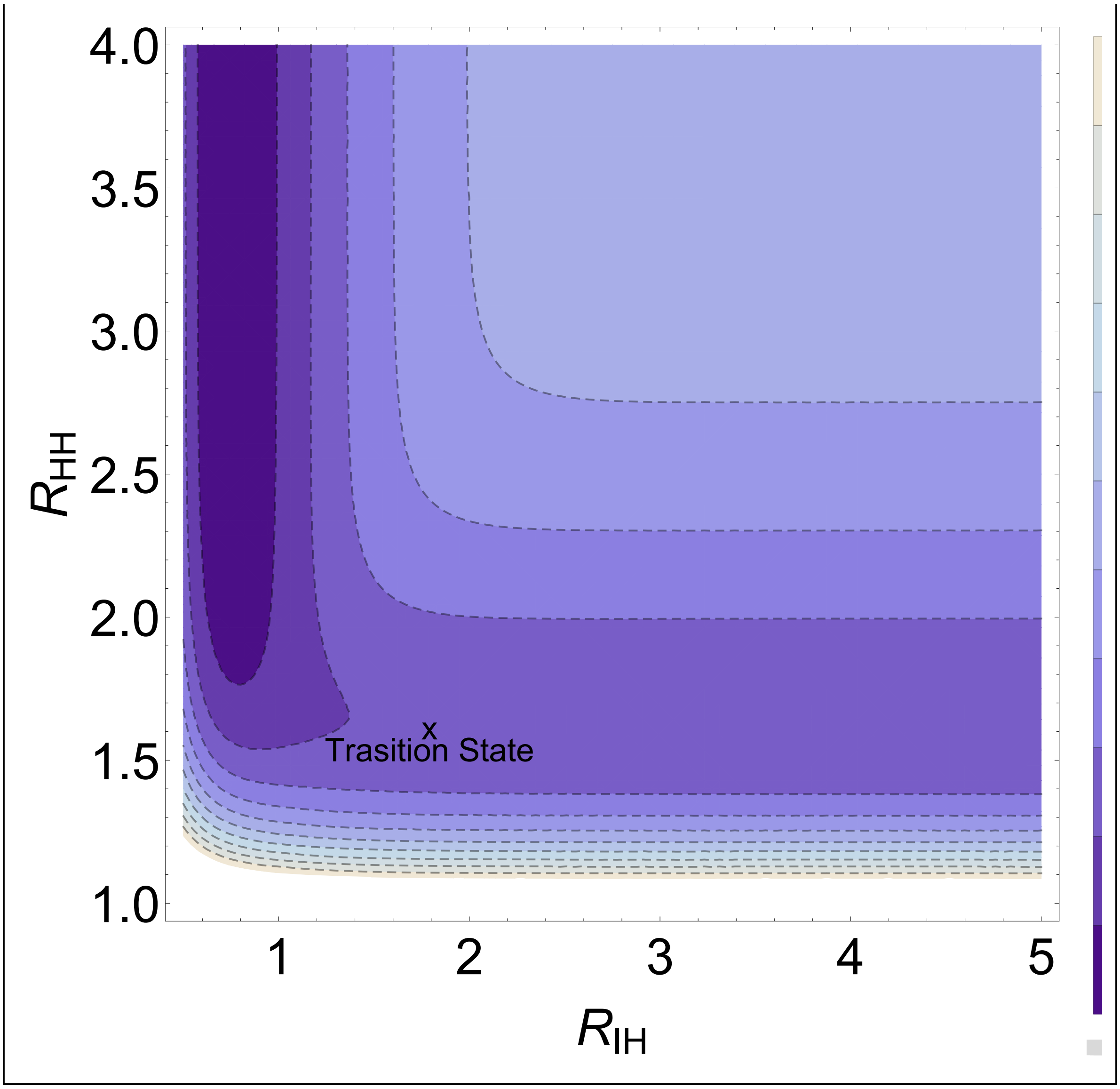
```
Clear[E1, Ephi, Eϕ, qai, qbj, qij, Jai, Jbj, Jij, Vij, k];
k = 0.17;
Dei = 458.39; Bi = 1.944; roi = 0.741;
Dej = 308.47; Bj = 1.751; roj = 1.609;
Deij = 308.47; Bij = 1.751; roij = 1.609;

E1[{ri_, rj_}] := (
   qai =
    (1/4) * Dei ((3 + k) * Exp[-2 * Bi * (ri - roi)] - (2 + 6 * k) * Exp[-Bi * (ri - roi)]);
   qbj = (1/4) * Dej ((3 + k) * Exp[-2 * Bj * (rj - roj)] -
       (2 + 6 * k) * Exp[-Bj * (rj - roj)]);
   qij = (1/4) * Deij ((3 + k) * Exp[-2 * Bij * (ri + rj - roij)] -
       (2 + 6 * k) * Exp[-Bij * (ri + rj - roij)]);
   Jai = (1/4) * Dei ((1 + 3 * k) * Exp[-2 * Bi * (ri - roi)] -
       (6 + 2 * k) * Exp[-Bi * (ri - roi)]);
   Jbj = (1/4) * Dej ((1 + 3 * k) * Exp[-2 * Bj * (rj - roj)] -
       (6 + 2 * k) * Exp[-Bj * (rj - roj)]);
   Jij = (1/4) * Deij ((1 + 3 * k) * Exp[-2 * Bij * (ri + rj - roij)] -
       (6 + 2 * k) * Exp[-Bij * (ri + rj - roij)]);
   Vij = (qai + qbj + qij - ((1/2) * ((Jai - Jbj)^2 + (Jbj - Jij)^2 + (Jij - Jai)^2))^
        (1/2)) / (1 + k)
  );
Ephi[{ri_, rj_, phi_}] := (
   qai =
    (1/4) * Dei ((3 + k) * Exp[-2 * Bi * (ri - roi)] - (2 + 6 * k) * Exp[-Bi * (ri - roi)]);
   qbj = (1/4) * Dej ((3 + k) * Exp[-2 * Bj * (rj - roj)] -
       (2 + 6 * k) * Exp[-Bj * (rj - roj)]);
   qij = (1/4) * Deij ((3 + k) * Exp[-2 * Bij *
           ((ri^2 + rj^2 - 2 * ri * rj * Cos[phi Degree])^(1/2) - roij)] - (2 + 6 * k) *
        Exp[-Bij * ((ri^2 + rj^2 - 2 * ri * rj * Cos[phi Degree])^(1/2) - roij)]);
   Jai = (1/4) * Dei ((1 + 3 * k) * Exp[-2 * Bi * (ri - roi)] -
       (6 + 2 * k) * Exp[-Bi * (ri - roi)]);
   Jbj = (1/4) * Dej ((1 + 3 * k) * Exp[-2 * Bj * (rj - roj)] -
       (6 + 2 * k) * Exp[-Bj * (rj - roj)]);
   Jij = (1/4) * Deij ((1 + 3 * k) * Exp[-2 * Bij *
           ((ri^2 + rj^2 - 2 * ri * rj * Cos[phi Degree])^(1/2) - roij)] - (6 + 2 * k) *
        Exp[-Bij * ((ri^2 + rj^2 - 2 * ri * rj * Cos[phi Degree])^(1/2) - roij)]);
   Vij = (qai + qbj + qij - ((1/2) * ((Jai - Jbj)^2 + (Jbj - Jij)^2 + (Jij - Jai)^2))^
        (1/2)) / (1 + k)
  );
```

```
Eϕ[{ri_, rj_, rk_}] := (
  qai =
   (1/4) * Dei ((3 + k) * Exp[-2 * Bi * (ri - roi)] - (2 + 6 * k) * Exp[-Bi * (ri - roi)]);
  qbj = (1/4) * Dej ((3 + k) * Exp[-2 * Bj * (rj - roj)] -
      (2 + 6 * k) * Exp[-Bj * (rj - roj)]);
  qij = (1/4) * Deij ((3 + k) * Exp[-2 * Bij * (rk - roij)] -
      (2 + 6 * k) * Exp[-Bij * (rk - roij)]);
  Jai = (1/4) * Dei ((1 + 3 * k) * Exp[-2 * Bi * (ri - roi)] -
      (6 + 2 * k) * Exp[-Bi * (ri - roi)]);
  Jbj = (1/4) * Dej ((1 + 3 * k) * Exp[-2 * Bj * (rj - roj)] -
      (6 + 2 * k) * Exp[-Bj * (rj - roj)]);
  Jij = (1/4) * Deij ((1 + 3 * k) * Exp[-2 * Bij * (rk - roij)] -
      (6 + 2 * k) * Exp[-Bij * (rk - roij)]);
  Vij = (qai + qbj + qij - ((1/2) * ((Jai - Jbj)^2 + (Jbj - Jij)^2 + (Jij - Jai)^2))^
       (1/2)) / (1 + k)
 )
```

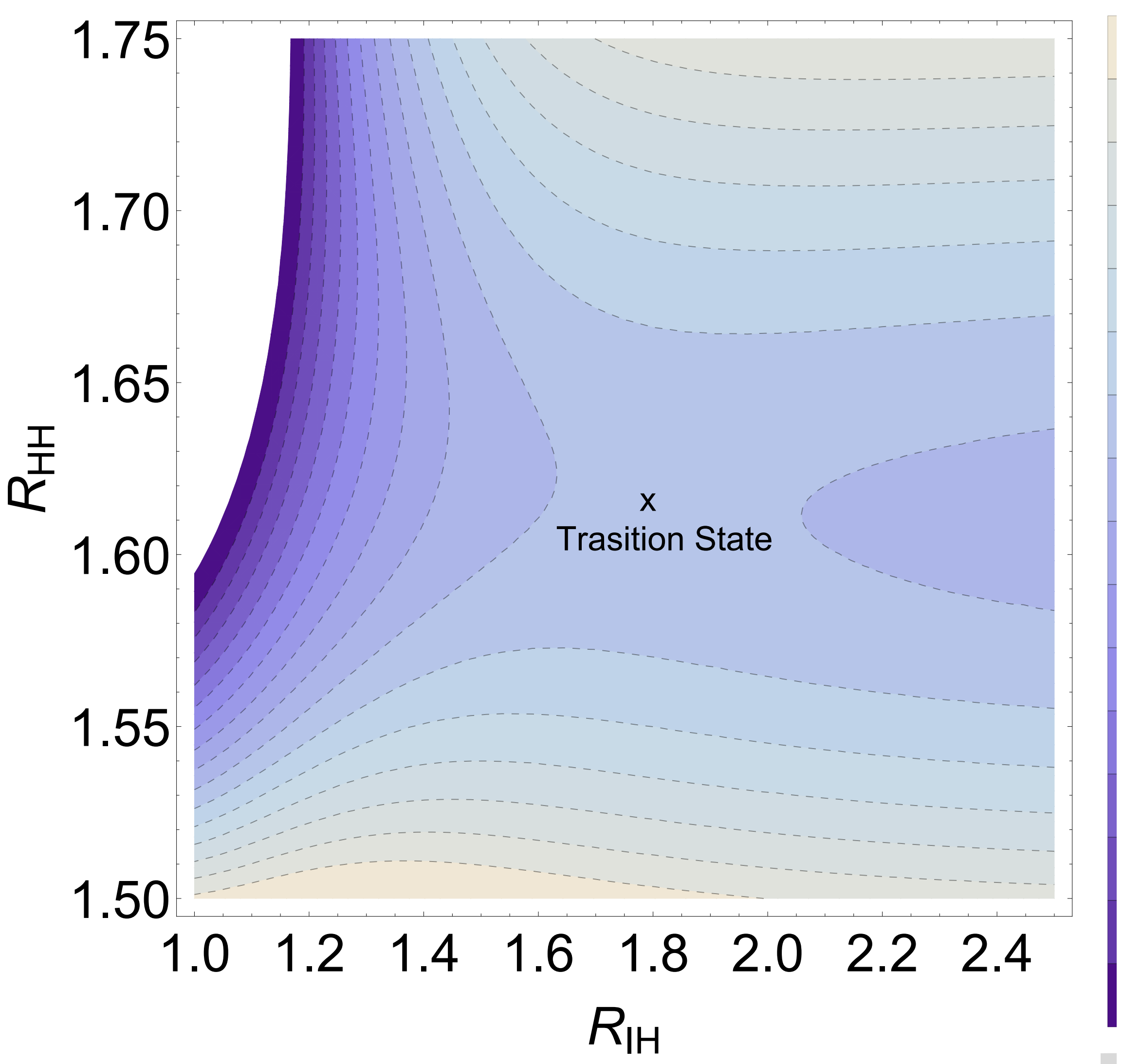
Contour Plot of the LEPS Potential

```
Show[ContourPlot[E1[{ri, rj}], {ri, 0.5, 5},
  {rj, 1.0, 4}, PlotTheme → "Scientific", Background → White,
  ContourStyle → Directive[GrayLevel[0], Opacity[0.4`], Dashing[{Small, Small}]],
  PlotLegends → Automatic, Contours → 10,
  ContourStyle → Directive[Black, Opacity[.3]],
  ColorFunction → "LakeColors", ImageSize → Large,
  LabelStyle → Directive[Black, 28, Background -> White], AxesLabel → {None, None},
  FrameLabel → {{HoldForm[R_HH], None}, {HoldForm[R_IH], None}}],
 Graphics[Style[Text["x",{1.791115996183624`, 1.6164728427573403`}],
   18, Background → None]], Graphics[Style[
   Text["Trasition State",{1.791115996183624`, 1.54}], 18, Background → None]]]
```

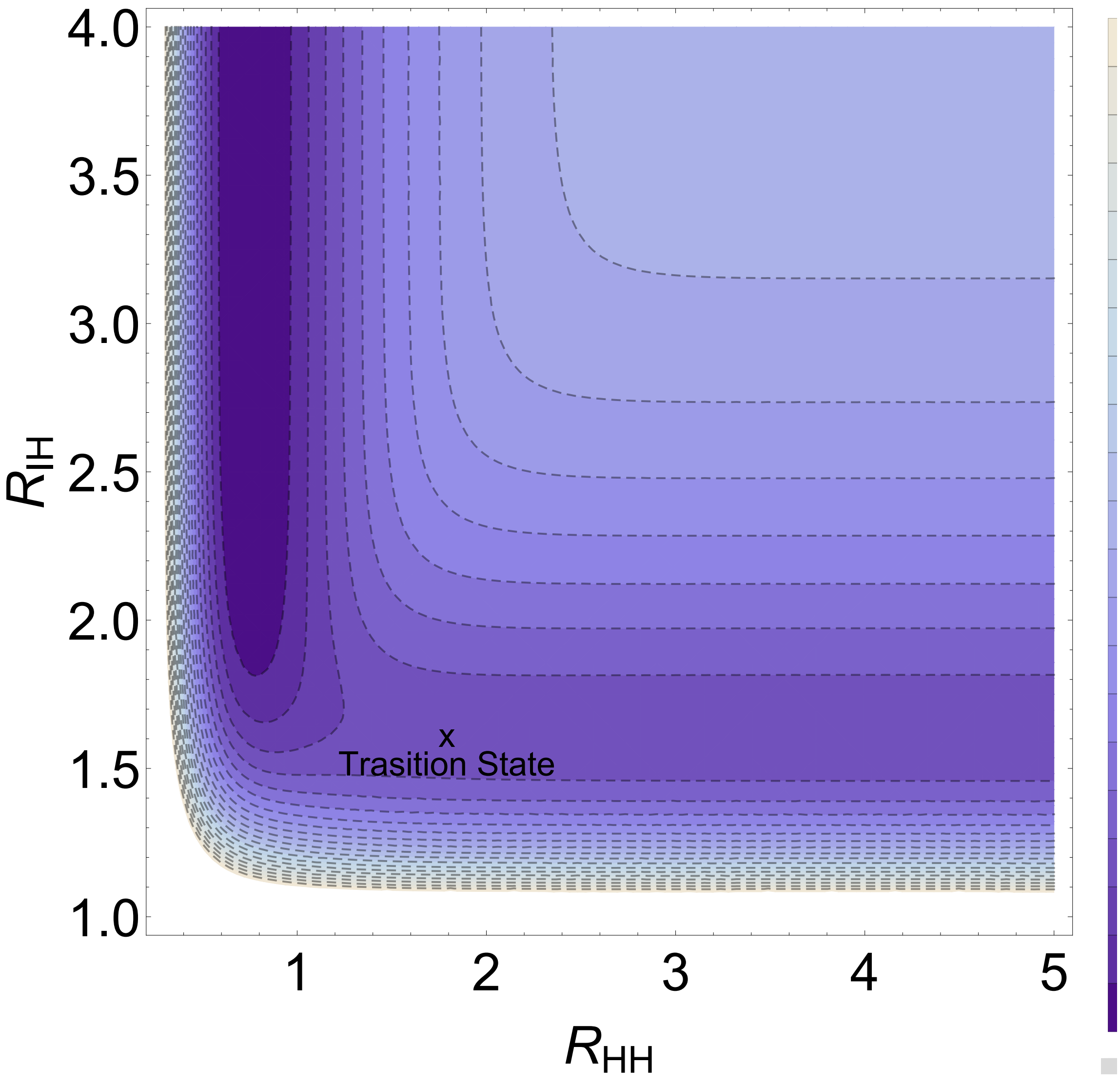


4.0
3.5
3.0
2.5
2.0
1.5
1.0
R_{HH}
x
Trasition State
1
2
3
4
5
R_{IH}

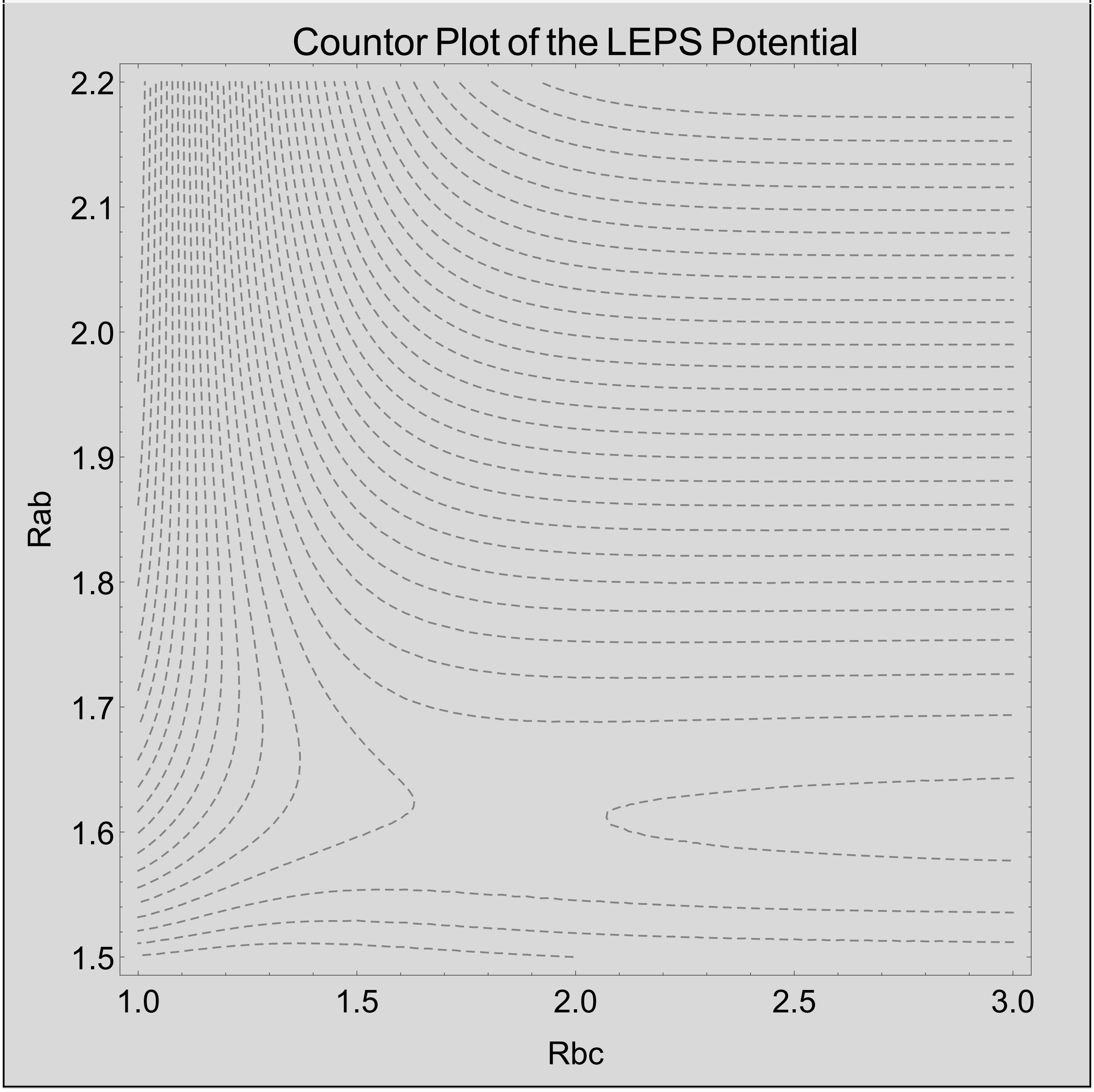
```
Show[ContourPlot[E1[{ri, rj}], {ri, 1.0, 2.5}, {rj, 1.5, 1.75}, Background → White,
  ContourStyle → Directive[GrayLevel[0], Opacity[0.4`], Dashing[{Small, Small}]],
  PlotLegends → Automatic, Contours → 15,
  ContourStyle → Directive[Black, Opacity[.3]], ColorFunction -> "LakeColors",
  ImageSize → Large, LabelStyle → Directive[Black, 28, Background -> White],
  FrameLabel → {{HoldForm[R_HH], None}, {HoldForm[R_IH], None}}], Graphics[Style[
   Text["x",{1.791115996183624`, 1.6164728427573403`}], 18, Background → None]],
 Graphics[Style[Text["Trasition State",{1.82, 1.605}], 18, Background → None]]]
```



```
Show[ContourPlot[E1[{ri, rj}], {ri, 0.3, 5},
  {rj, 1.0, 4}, PlotTheme → "Scientific", Background → White,
  ContourStyle → Directive[GrayLevel[0], Opacity[0.4`], Dashing[{Small, Small}]],
  PlotLegends → Automatic, Contours → 20,
  ContourStyle → Directive[White, Opacity[.3]],
  ColorFunction → "LakeColors", ImageSize → Large,
  LabelStyle → Directive[Black, 28, Background -> White], AxesLabel → {None, None},
  FrameLabel → {{HoldForm[R_IH], None}, {HoldForm[R_HH], None}}],
 Graphics[Style[Text["x",{1.791115996183624`, 1.6164728427573403`}],
   18, Background → None]], Graphics[Style[
   Text["Trasition State",{1.791115996183624`, 1.52}], 18, Background → None]]]
```

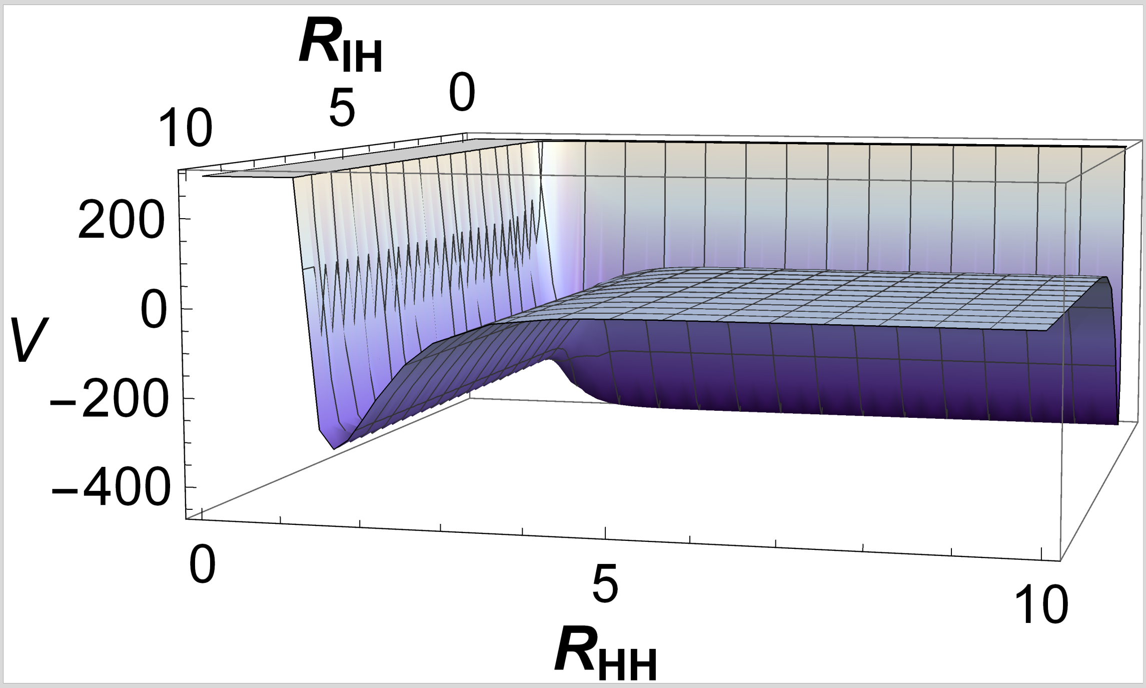


```
Show[ContourPlot[E1[{ri, rj}],
  {ri, 1.0, 3}, {rj, 1.5, 2.2}, PlotTheme → "Scientific",
  ContourStyle → Directive[GrayLevel[0], Opacity[0.4], Dashing[{Small, Small}]],
  ContourShading → False, Contours → 40, PlotPoints → 10, AxesLabel → {None, None},
  FrameLabel → {{HoldForm[Rab], None}, {HoldForm[Rbc], None}},
  PlotLabel → HoldForm[Countor Plot of the LEPS Potential],
  LabelStyle → {18, GrayLevel[0]}, ImageSize → Large, ColorFunction → "Rainbow"]]
```

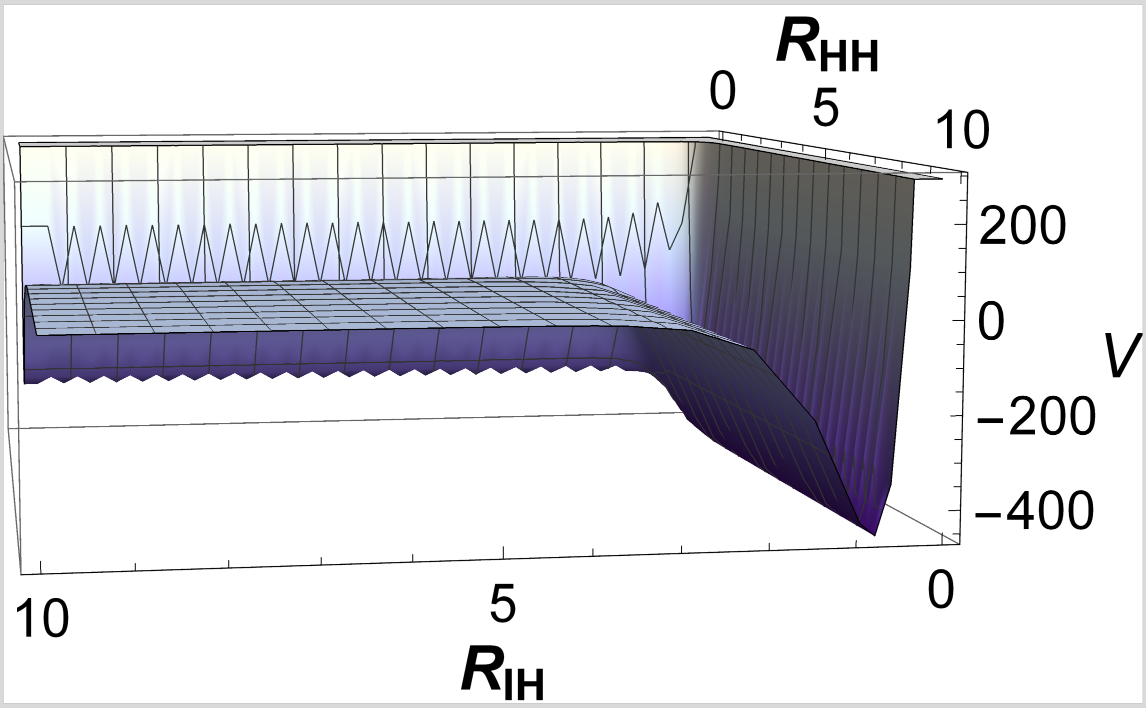


3 D Plot of the LEPS Potential

```
plot = Plot3D[E1[{ri, rj}], {ri, 0, 10},
   {rj, 0, 10}, ColorFunction → "LakeColors", ImageSize → Full];
Show[plot, AxesLabel → {Style["RIH", FontSize → 32],
   Style["RHH", FontSize → 32], Style["V", FontSize → 32]},
 AxesStyle → Directive[Black, 28], Background → White]
```



```
plot = Plot3D[E1[{ri, rj}], {ri, 0, 10},
   {rj, 0, 10}, ColorFunction → "LakeColors", ImageSize → Full];
Show[plot, AxesLabel → {Style["R_IH", FontSize → 32],
   Style["R_HH", FontSize → 32], Style["V", FontSize → 32]},
 AxesStyle → Directive[Black, 28], Background → White]
```



Force Constants

```
F11[xts_, inc_, nstep_] := Module[{i},
   X0 = N[xts];
   xinc = {inc, 0};
   sum0 = 0;
   Print[""];
   Print["Calculation of the Force Constant F11"];
   Print["      ", "Coordinates = ", PaddedForm[X0, {8, 8}],
    "      ", "V-V* = ", PaddedForm[dV = E1[X0] - E1[xts], {8, 8}]];
   For[i = 1, i <= nstep, i++,
    Xi = X0 + xinc;
    dV = E1[Xi] - E1[xts];
    dVinc = dV / (Part[Xi, 1] - Part[xts, 1]) ^2;
    sumf = sum0 + dVinc;
    Print["      ", "Coordinates = ",
     PaddedForm[Xi, {8, 8}], "      ", "V-V* = ", PaddedForm[dV, {8, 8}],
     "     ", "(V-V*)/r^2 =  ", PaddedForm[dVinc, {8, 8}]];
    X0 = Xi;
    sum0 = sumf;
   ];
   Print[
    "                                                                                ",
    "Mean = ", sum0 / nstep];
   Print[
```

```
    "                                                                                          ",
    "F11 = ",
    2 * sum0 / nstep];
   Return[2 * sum0 / nstep];
  ];
F22[xts_, inc_, nstep_] := Module[{i},
   X0 = N[xts];
   xinc = {0, inc};
   sum0 = 0;
   Print[""];
   Print["Calculation of the Force Constant F22"];
   Print["     ", "Coordinates = ", PaddedForm[X0, {8, 8}],
    "     ", "V-V* = ", PaddedForm[dV = E1[X0] - E1[xts], {8, 8}]];
   For[i = 1, i <= nstep, i++,
    Xi = X0 + xinc;
    dV = E1[Xi] - E1[xts];
    dVinc = dV / (Part[Xi, 2] - Part[xts, 2]) ^2;
    sumf = sum0 + dVinc;
    Print["     ", "Coordinates = ",
     PaddedForm[Xi, {8, 8}], "     ", "V-V* = ", PaddedForm[dV, {8, 8}],
     "    ", "(V-V*)/r^2 =  ", PaddedForm[dVinc, {8, 8}]];
    sum0 = sumf;
    X0 = Xi;
   ];
   Print[
    "                                                                                          ",
    "Mean = ", sum0 / nstep];
   Print[
    "                                                                                          ",
    "F22 = ",
    2 * sum0 / nstep];
   Return[2 * sum0 / nstep];
  ];
Fc[xts_, inc_, nstep_] := Module[{i},
   X0 = N[xts];
   xinc = {inc, inc};
   sum0 = 0;
   Print[""];
   Print["Calculation of the Force Constant Fc"];
   Print["     ", "Coordinates = ", PaddedForm[X0, {8, 8}],
    "     ", "V-V* = ", PaddedForm[dV = E1[X0] - E1[xts], {8, 8}]];
   For[i = 1, i <= nstep, i++,
    Xi = X0 + xinc;
    dV = E1[Xi] - E1[xts];
    dVinc = dV / ((Part[Xi, 2] - Part[xts, 2]) ^2 + (Part[Xi, 1] - Part[xts, 1]) ^2);
    sumf = sum0 + dVinc;
    Print["     ", "Coordinates = ",
     PaddedForm[Xi, {8, 8}], "     ", "V-V* = ", PaddedForm[dV, {8, 8}],
     "    ", "(V-V*)/r^2 =  ", PaddedForm[dVinc, {8, 8}]];
    X0 = Xi;
    sum0 = sumf;
   ];
   Print[
    "                                                                                          ",
```

```
    "Mean = ", sum0 / nstep];
   Print[
    "                                                                                ",
    "Fc = ",
    2 * sum0 / nstep];
   Return[2 * sum0 / nstep];
  ];
Fphi[xts_, nstep_, inc_] := Module[{i},
   q = nstep / inc;
   R30 = ((Part[xts, 1])^2 + (Part[xts, 2])^2 -
       2 * (Part[xts, 1]) * (Part[xts, 2]) * Cos[(180) Degree])^(1 / 2);
   X0 = ArrayReshape[xnew = {xts, R30}, 3];
   sum0 = 0;
   Print[""];
   Print["Calculation of the Force Constant Fϕ"];
   For[i = inc, i <= nstep, i = i + 2,
    R3 = ((Part[xts, 1])^2 + (Part[xts, 2])^2 -
        2 * (Part[xts, 1]) * (Part[xts, 2]) * Cos[(180 - i) Degree])^(1 / 2);
    Xi = ArrayReshape[xnew = {xts, R3}, 3];
    irad = i * π / 180;
    dV = Eϕ[Xi] - Eϕ[X0];
    dVinc = dV / irad^2;
    sumf = sum0 + dVinc;
    Print["     ", "ϕ (deg/rad) = (", PaddedForm[i, 2],
     " /", PaddedForm[N[irad], {8, 8}], " )", "     ", "RAC = ",
     PaddedForm[R3, {8, 8}], "     ", "V-V* =  ", PaddedForm[dV, {8, 8}],
     "     ", "(V-V*)/r^2 =  ", PaddedForm[dVinc, {8, 8}]];
    sum0 = sumf;
   ];
   Print[
    "                                                                                ",
    "Mean = ", sum0 / q];
   Print[
    "                                                                                ",
    "Fϕ = ",
    2 * sum0 / q];
   Return[2 * sum0 / q];
  ];
```

```
FCalc[x0_, StepSize_, MaxNIter_, MaxPhiIter_, PhiStep_, M1_, M2_, M3_] := Module[{},
   TS = N[x0];
   ForceF11 = F11[TS, StepSize, MaxNIter];
   ForceF22 = F22[TS, StepSize, MaxNIter];
   ForceFc = Fc[TS, StepSize, MaxNIter];
   ForceF12 = (1 / 2) * (2 * ForceFc - ForceF11 - ForceF22);
   Print["Calculation of the Force Constant F12"];
   Print["     ", Subscript[F, 12], " = 1/2 (2",
    Subscript[F, c], "-", Subscript[F, 11], "-", Subscript[F, 22], ")"];
   Print["     ", Subscript[F, 12], " = ", ForceF12];
   ForceFphi = Fphi[TS, MaxPhiIter, PhiStep];
   Print[""];
   Print["Summary of the Force Constants"];
   Print["     ", Subscript[F, 11], " = ", PaddedForm[ForceF11, {8, 4}]];
   Print["     ", Subscript[F, 22], " = ", PaddedForm[ForceF22, {8, 4}]];
   Print["     ", Subscript[F, c], "  = ", PaddedForm[ForceFc, {8, 4}]];
   Print["     ", Subscript[F, 12], " = ", PaddedForm[ForceF12, {8, 4}]];
   Print["     ", Subscript[F, ϕ], "  = ", PaddedForm[ForceFphi, {8, 4}]];
   Print[""];
   Print["Optimized Geometry"];
   Print["     ", "Coordinates = ", TS];
   Print["     ", "Energy = ", E1[TS]];
   Return[Freq];
  ];
```

Numerical Differentiation by Newton - Raphson Method

```
NumDiff[x0_, h_] := Module[{},
   Print["Current Coordinates =", x0];
   Print[""];
   xstep = {h, 0};
   ystep = {0, h};
   Print["Gradient"];
   fxs = E1[x0 + xstep];
   Print["f(1,0)  = ", fxs];
   fxd = E1[x0 - xstep];
   Print["f(-1,0)  = ", fxd];
   gx = (1 / (2 * h)) * (fxs - fxd);
   Print["gx = ", gx];
   Print[""];
   fys = E1[x0 + ystep];
   Print["f(0,1)  = ", fys];
   fyd = E1[x0 - ystep];
   Print["f(0,-1)  = ", fyd];
   gy = (1 / (2 * h)) * (fys - fyd);
   Print["gy = ", gy];
   Print[""];
   Print["Hessian"];
   fxx = (E1[x0 + xstep] - 2 E1[x0] + E1[x0 - xstep]) / (h^2);
   Print["Hxx = ", fxx];
   fyy = (E1[x0 + ystep] - 2 E1[x0] + E1[x0 - ystep]) / (h^2);
```

```
    Print["Hyy = ", fyy];
    fxy = (E1[x0 + xstep + ystep] - E1[x0 + xstep - ystep] -
        E1[x0 - xstep + ystep] + E1[x0 - xstep - ystep]) / (4 * (h^2));
    Print["Hxy = ", fxy];

    Print[""];
    Print["Hessian Matrix"];
    Ho = {{fxx, fxy}, {fxy, fyy}};
    Print["Hessian = H = ", Ho];
    Hi = Eigenvalues[Ho];
    Print["Eigenvalues = ", Hi];
    Hin = Inverse[Ho];
    Print["H^-1 =", Hin];
    g = {gx, gy};
    Print["Gradient =", g];
    xf = x0 - Hin.g;
    Print["xf = ", x0, "-", Hin, g];
    Print[""];
    Print["New Coordinates = ", "xf = ", xf];
    Print[""];
    Return[xf];
   ];

TSOpt[x0_, h_, max_, tol_] := Module[{i},
    P0 = N[x0];
    count = 0;
    xstep = {h, 0};
    ystep = {0, h};
    Print["Optimization Process"];
    While[Abs[(1 / (2 * h)) * (E1[P0 + xstep] - E1[P0 - xstep])] > tol &&
      Abs[(1 / (2 * h)) * (E1[P0 + ystep] - E1[P0 - ystep])] > tol,
     Print["Step #", count + 1];
     P1 = NumDiff[P0, h];
     P0 = P1;
     count++;
     If[count == max, Break[]];
    ];
    Print["Stationary Point"];
    Print["Current Coordinates =", P1];
    Print["Gradient"];
    fxs = E1[P1 + xstep];
    Print["f(1,0) = ", fxs];
    fxd = E1[P1 - xstep];
    Print["f(-1,0) = ", fxd];
    gx = (1 / (2 * h)) * (fxs - fxd);
    Print["gx = ", gx];
    Print[""];
    fys = E1[P1 + ystep];
    Print["f(0,1) = ", fys];
    fyd = E1[P1 - ystep];
    Print["f(0,-1) = ", fyd];
    gy = (1 / (2 * h)) * (fys - fyd);
    Print["gy = ", gy];
    Print[""];
```

```
    Print[""];
    Print["Hessian"];
    fxx = (E1[P1 + xstep] - 2 E1[P1] + E1[P1 - xstep]) / (h^2);
    Print["Hxx = ", fxx];
    fyy = (E1[P1 + ystep] - 2 E1[P1] + E1[P1 - ystep]) / (h^2);
    Print["Hyy = ", fyy];
    fxy = (E1[P1 + xstep + ystep] - E1[P1 + xstep - ystep] -
        E1[P1 - xstep + ystep] + E1[P1 - xstep - ystep]) / (4 * (h^2));
    Print["Hxy = ", fxy];

    Print[""];
    Print["Hessian Matrix"];
    Ho = {{fxx, fxy}, {fxy, fyy}};
    Print["Hessian = H = ", Ho];
    Hi = Eigenvalues[Ho];
    Print["Eigenvalues = ", Hi];
    Hin = Inverse[Ho];
    Print["H^-1 =", Hin];
    g = {gx, gy};
    Print["Gradient =", g];
    Return[xf];
   ];
```

```
x0 = {1.5, 1.8};
h = 0.01;
tol = 1 * 10^-5;
max = 10;
T = 300;
A1 = 1.008;
A2 = 1.008;
A3 = 79.90;
vAB = 2649.0;
dAB = 1.414;

u1 = ((A1 * A1) / (A1 + A2)) * 10^-3;
u2 = ((A2 * A3) / (A2 + A3)) * 10^-3;
u3 = ((A1 * A3) / (A1 + A3)) * 10^-3;
rAB = dAB * 100 * 10^-12;
wAB = 2649.0 * 2.9979 * 10^10;
xn = TSOpt[x0, h, max, tol];
Rij = Part[xn, 1] * 10^-12 * 100;
Rjk = Part[xn, 2] * 10^-12 * 100;
vTS = FCalc[xn, 0.01, 5, 10, 2, u1, u2, u3];
```

```
Optimization Process

Step #1

Current Coordinates ={1.5, 1.8}


Gradient

f(1,0) = -292.442

f(-1,0) = -293.48
```

gx = 51.9209

f(0,1) = −291.345

f(0,−1) = −294.506

gy = 158.014

Hessian

Hxx = −242.792

Hyy = 468.224

Hxy = 250.377

Hessian Matrix

Hessian = H = {{−242.792, 250.377}, {250.377, 468.224}}

Eigenvalues = {547.542, −322.111}

H^{-1} ={{−0.00265479, 0.00141961}, {0.00141961, 0.00137661}}

Gradient ={51.9209, 158.014}

xf = {1.5, 1.8}−{{−0.00265479, 0.00141961}, {0.00141961, 0.00137661}}{51.9209, 158.014}

New Coordinates = xf = {1.41352, 1.50877}

Step #2

Current Coordinates ={1.41352, 1.50877}

Gradient

f(1,0) = −292.239

f(−1,0) = −292.187

gx = −2.57113

f(0,1) = −295.06

f(0,−1) = −289.058

gy = −300.095

Hessian

Hxx = −36.7697

Hyy = 3042.81

Hxy = 210.76

Hessian Matrix

Hessian = H = {{−36.7697, 210.76}, {210.76, 3042.81}}

Eigenvalues = {3057.17, -51.1267}

H^{-1} ={{-0.0194674, 0.00134841}, {0.00134841, 0.000235246}}

Gradient ={-2.57113, -300.095}

xf = {1.41352, 1.50877}-
{{-0.0194674, 0.00134841}, {0.00134841, 0.000235246}}{-2.57113, -300.095}

New Coordinates = xf = {1.76812, 1.58283}

Step #3

Current Coordinates ={1.76812, 1.58283}

Gradient

f(1,0) = -305.772

f(-1,0) = -305.741

gx = -1.56317

f(0,1) = -306.324

f(0,-1) = -304.974

gy = -67.5232

Hessian

Hxx = -10.1849

Hyy = 2146.89

Hxy = 56.3609

Hessian Matrix

Hessian = H = {{-10.1849, 56.3609}, {56.3609, 2146.89}}

Eigenvalues = {2148.37, -11.6566}

H^{-1} ={{-0.0857299, 0.0022506}, {0.0022506, 0.000406706}}

Gradient ={-1.56317, -67.5232}

xf = {1.76812, 1.58283}-
{{-0.0857299, 0.0022506}, {0.0022506, 0.000406706}}{-1.56317, -67.5232}

New Coordinates = xf = {1.78608, 1.61381}

Step #4

Current Coordinates ={1.78608, 1.61381}

Gradient

f(1,0) = -306.866

f(−1,0) = −306.865

gx = −0.0675232

f(0,1) = −306.824

f(0,−1) = −306.722

gy = −5.09833

Hessian

Hxx = −15.4479

Hyy = 1824.58

Hxy = 55.1328

Hessian Matrix

Hessian = H = {{−15.4479, 55.1328}, {55.1328, 1824.58}}

Eigenvalues = {1826.23, −17.0984}

H^{-1} ={{−0.0584322, 0.00176563}, {0.00176563, 0.00049472}}

Gradient ={−0.0675232, −5.09833}

xf = {1.78608, 1.61381}−
{{−0.0584322, 0.00176563}, {0.00176563, 0.00049472}}{−0.0675232, −5.09833}

New Coordinates = xf = {1.79113, 1.61645}

Step ⌗5

Current Coordinates ={1.79113, 1.61645}

Gradient

f(1,0) = −306.872

f(−1,0) = −306.872

gx = −0.00131633

f(0,1) = −306.781

f(0,−1) = −306.781

gy = −0.0349577

Hessian

Hxx = −15.4859

Hyy = 1799.27

Hxy = 54.2427

Hessian Matrix

Hessian = H = {{-15.4859, 54.2427}, {54.2427, 1799.27}}

Eigenvalues = {1800.89, -17.1058}

H^{-1} ={{-0.0584072, 0.00176081}, {0.00176081, 0.000502699}}

Gradient ={-0.00131633, -0.0349577}

xf = {1.79113, 1.61645}-
{{-0.0584072, 0.00176081}, {0.00176081, 0.000502699}}{-0.00131633, -0.0349577}

New Coordinates = xf = {1.79112, 1.61647}

Stationary Point

Current Coordinates ={1.79112, 1.61647}

Gradient

f(1,0) = -306.872

f(-1,0) = -306.872

gx = 8.06153×10^{-8}

f(0,1) = -306.781

f(0,-1) = -306.781

gy = 4.79476×10^{-6}

Hessian

Hxx = -15.492

Hyy = 1799.07

Hxy = 54.2479

Hessian Matrix

Hessian = H = {{-15.492, 54.2479}, {54.2479, 1799.07}}

Eigenvalues = {1800.69, -17.1124}

H^{-1} ={{-0.0583846, 0.00176049}, {0.00176049, 0.000502758}}

Gradient ={8.06153×10^{-8}, 4.79476×10^{-6}}

Calculation of the Force Constant F11

Coordinates = { 1.79111600, 1.61647280} V-V* = 0.00000000

Coordinates = { 1.80111600, 1.61647280}
V-V* = -0.00077460 (V-V*)/r^2 = -7.74601070

Coordinates = { 1.81111600, 1.61647280}
V-V* = -0.00299194 (V-V*)/r^2 = -7.47984540

```
Coordinates = { 1.82111600,  1.61647280}
 V−V* = −0.00655133    (V−V*)/r^2 =  −7.27925570
Coordinates = { 1.83111600,  1.61647280}
 V−V* = −0.01135760    (V−V*)/r^2 =  −7.09850030
Coordinates = { 1.84111600,  1.61647280}
 V−V* = −0.01732081    (V−V*)/r^2 =  −6.92832310
                                                        Mean = −7.30639
                                                        F11 = −14.6128
```

Calculation of the Force Constant F22

```
Coordinates = { 1.79111600,  1.61647280}     V−V* =  0.00000000
Coordinates = { 1.79111600,  1.62647280}
 V−V* =  0.08995359    (V−V*)/r^2 =   899.53593000
Coordinates = { 1.79111600,  1.63647280}
 V−V* =  0.35030179    (V−V*)/r^2 =   875.75447000
Coordinates = { 1.79111600,  1.64647280}
 V−V* =  0.77191151    (V−V*)/r^2 =   857.67945000
Coordinates = { 1.79111600,  1.65647280}
 V−V* =  1.34601500    (V−V*)/r^2 =   841.25938000
Coordinates = { 1.79111600,  1.66647280}
 V−V* =  2.06419630    (V−V*)/r^2 =   825.67851000
                                                        Mean = 859.982
                                                        F22 = 1719.96
```

Calculation of the Force Constant Fc

```
Coordinates = { 1.79111600,  1.61647280}     V−V* =  0.00000000
Coordinates = { 1.80111600,  1.62647280}
 V−V* =  0.09453741    (V−V*)/r^2 =   472.68703000
Coordinates = { 1.81111600,  1.63647280}
 V−V* =  0.36849379    (V−V*)/r^2 =   460.61724000
Coordinates = { 1.82111600,  1.64647280}
 V−V* =  0.81247890    (V−V*)/r^2 =   451.37716000
Coordinates = { 1.83111600,  1.65647280}
 V−V* =  1.41748380    (V−V*)/r^2 =   442.96368000
Coordinates = { 1.84111600,  1.66647280}
 V−V* =  2.17486650    (V−V*)/r^2 =   434.97330000
                                                        Mean = 452.524
                                                        Fc = 905.047
```

Calculation of the Force Constant F12

$$F_{12} = \frac{1}{2}(2F_c - F_{11} - F_{22})$$

$F_{12} = 52.3722$

Calculation of the Force Constant Fϕ

```
   ϕ (deg/rad) = (  2 / 0.03490659 )     RAC =
 3.40707120    V-V* =   0.00341217    (V-V*)/r^2 =   2.80037070
   ϕ (deg/rad) = (  4 / 0.06981317 )     RAC =
 3.40551850    V-V* =   0.01366562    (V-V*)/r^2 =   2.80385000
   ϕ (deg/rad) = (  6 / 0.10471976 )     RAC =
 3.40293110    V-V* =   0.03081137    (V-V*)/r^2 =   2.80966010
   ϕ (deg/rad) = (  8 / 0.13962634 )     RAC =
 3.39931000    V-V* =   0.05493481    (V-V*)/r^2 =   2.81781800
   ϕ (deg/rad) = ( 10 / 0.17453293 )     RAC =
 3.39465610    V-V* =   0.08615639    (V-V*)/r^2 =   2.82834760
                                                            Mean = 2.81201
                                                            Fϕ = 5.62402
```

Summary of the Force Constants

F_{11} = −14.6128

F_{22} = 1719.9631

F_c = 905.0474

F_{12} = 52.3722

F_ϕ = 5.6240

Optimized Geometry

Coordinates = {1.79112, 1.61647}

Energy = −306.871

Analytic Optimization

```
Hess[x0_] := Module[{},
  gri[{ri_, rj_}] = ∂ri E1[{ri, rj}];
  gx = gri[x0];
  grj[{ri_, rj_}] = ∂rj E1[{ri, rj}];
  gy = grj[x0];
  hxx[{ri_, rj_}] = ∂ri,ri E1[{ri, rj}];
  Hxx = hxx[x0];
  hxy[{ri_, rj_}] = ∂ri,rj E1[{ri, rj}];
  Hxy = hxy[x0];
  hyy[{ri_, rj_}] = ∂rj,rj E1[{ri, rj}];
  Hyy = hyy[x0];
  Hyx = Hxy;
  H = ( Hxx  Hxy
        Hyx  Hyy );
  Hin = Inverse[H];
  Heign = Eigenvalues[H];
  G = {gx, gy};
  nextX = x0 - Hin.G;

  Print["     ", "Current Coordinate = ", x0, "   ", "Energy = ", E1[x0]];
  Print["     ", "Eigenvalues = ", Heign, "      ", "Gradient =", G];
  Print["     ", "Force Constants = ", H];
```

```
  Print["     ", "New Coordinate = ", nextX];
  Return[nextX];
 ]
HessDev[x0_] := Module[{},
  gri[{ri_, rj_}] = ∂ri E1[{ri, rj}];
  gx = gri[x0];
  grj[{ri_, rj_}] = ∂rj E1[{ri, rj}];
  gy = grj[x0];
  hxx[{ri_, rj_}] = ∂ri,ri E1[{ri, rj}];
  Hxx = hxx[x0];
  hxy[{ri_, rj_}] = ∂ri,rj E1[{ri, rj}];
  Hxy = hxy[x0];
  hyy[{ri_, rj_}] = ∂rj,rj E1[{ri, rj}];
  Hyy = hyy[x0];
  H = {Hxx, Hxy, Hyy, Heign, gx, gy};
  Return[H];
 ]

AnalyticOptimize[x0_, max_, tol_] := Module[{},
   P0 = N[x0];
   Print[Optimization Process];
   gri[{ri_, rj_}] = ∂ri E1[{ri, rj}];
   grj[{ri_, rj_}] = ∂rj E1[{ri, rj}];
   count = 0;
   While[Abs[gri[P0]] > tol && Abs[grj[P0]] > tol,
    Print["Step #", count + 1];
    P1 = Hess[P0];
    P0 = P1;
    count++;
    If[count == max, Break[]];
   ];
   Print["Step #", count + 1];
   Hess[P1];
   Return[P1];
  ];
```

```
x0 = {1.5, 1.8};
AnalyticOptimize[x0, 5, 1 * 10^-5];
```

```
Optimization Process
Step ⌗1
    Current Coordinate = {1.5, 1.8}   Energy = -292.949
    Eigenvalues = {547.367, -322.083}      Gradient ={51.9049, 158.091}
    Force Constants = {{-242.773, 250.331}, {250.331, 468.058}}
    New Coordinate = {1.41332, 1.5086}
Step ⌗2
    Current Coordinate = {1.41332, 1.5086}   Energy = -292.159
    Eigenvalues = {3059.22, -51.0229}      Gradient ={-2.60469, -300.408}
    Force Constants = {{-36.6698, 210.798}, {210.798, 3044.87}}
    New Coordinate = {1.76821, 1.58269}
Step ⌗3
    Current Coordinate = {1.76821, 1.58269}   Energy = -305.747
    Eigenvalues = {2149.6, -11.6067}      Gradient ={-1.57374, -67.6411}
    Force Constants = {{-10.1388, 56.3049}, {56.3049, 2148.13}}
    New Coordinate = {1.78536, 1.61373}
Step ⌗4
    Current Coordinate = {1.78536, 1.61373}   Energy = -306.864
    Eigenvalues = {1826.67, -17.1599}      Gradient ={-0.0630432, -5.1293}
    Force Constants = {{-15.5019, 55.2653}, {55.2653, 1825.02}}
    New Coordinate = {1.79074, 1.61637}
Step ⌗5
    Current Coordinate = {1.79074, 1.61637}   Energy = -306.871
    Eigenvalues = {1801.29, -17.1297}      Gradient ={-0.00129306, -0.0362169}
    Force Constants = {{-15.5066, 54.303}, {54.303, 1799.66}}
    New Coordinate = {1.79072, 1.61639}
Step ⌗6
    Current Coordinate = {1.79072, 1.61639}   Energy = -306.871
    Eigenvalues = {1801.09, -17.1359}      Gradient ={8.01067×10^-8, -2.07281×10^-6}
    Force Constants = {{-15.5124, 54.3075}, {54.3075, 1799.46}}
    New Coordinate = {1.79072, 1.61639}
```

Optimization of Products

```
x0 = {0.5, 3};
AnalyticOptimize[x0, 20, 1 * 10^-5];
```

```
Optimization Process
Step ⌗1
    Current Coordinate = {0.5, 3.}   Energy = -292.301
    Eigenvalues = {12152.4, 18.0461}      Gradient ={-1703.81, -6.21372}
```

```
        Force Constants = {{12152.4, 6.83911}, {6.83911, 18.05}}
        New Coordinate = {0.640039, 3.29119}
    Step ⌗2
        Current Coordinate = {0.640039, 3.29119}   Energy = -435.81
        Eigenvalues = {6044.59, 6.23101}      Gradient ={-471.186, -2.38028}
        Force Constants = {{6044.59, 2.6317}, {2.6317, 6.23216}}
        New Coordinate = {0.717839, 3.64027}
    Step ⌗3
        Current Coordinate = {0.717839, 3.64027}   Energy = -456.971
        Eigenvalues = {3958.07, 2.14535}      Gradient ={-86.1866, -0.9296}
        Force Constants = {{3958.07, 0.906752}, {0.906752, 2.14556}}
        New Coordinate = {0.739517, 4.06438}
    Step ⌗4
        Current Coordinate = {0.739517, 4.06438}   Energy = -458.197
        Eigenvalues = {3494.77, 0.746741}      Gradient ={-5.26857, -0.36293}
        Force Constants = {{3494.77, 0.265186}, {0.265186, 0.746761}}
        New Coordinate = {0.740988, 4.54986}
    Step ⌗5
        Current Coordinate = {0.740988, 4.54986}   Energy = -458.314
        Eigenvalues = {3464.93, 0.264415}      Gradient ={-0.0783199, -0.139453}
        Force Constants = {{3464.93, 0.0758836}, {0.0758836, 0.264416}}
        New Coordinate = {0.740999, 5.07726}
    Step ⌗6
        Current Coordinate = {0.740999, 5.07726}   Energy = -458.36
        Eigenvalues = {3464.68, 0.09532}      Gradient ={-0.0167865, -0.0526157}
        Force Constants = {{3464.68, 0.0234695}, {0.0234695, 0.0953202}}
        New Coordinate = {0.741, 5.62925}
    Step ⌗7
        Current Coordinate = {0.741, 5.62925}   Energy = -458.379
        Eigenvalues = {3464.65, 0.0347559}      Gradient ={-0.00513091, -0.0195856}
        Force Constants = {{3464.65, 0.00789422}, {0.00789422, 0.034756}}
        New Coordinate = {0.741, 6.19276}
    Step ⌗8
        Current Coordinate = {0.741, 6.19276}   Energy = -458.386
        Eigenvalues = {3464.64, 0.0127411}      Gradient ={-0.00169209, -0.00723983}
        Force Constants = {{3464.64, 0.00279466}, {0.00279466, 0.0127411}}
        New Coordinate = {0.741, 6.76099}
    Step ⌗9
        Current Coordinate = {0.741, 6.76099}   Energy = -458.388
```

Eigenvalues = {3464.64, 0.00468095}   Gradient ={-0.000592073, -0.00266829}

Force Constants = {{3464.64, 0.00101275}, {0.00101275, 0.00468095}}

New Coordinate = {0.741, 7.33102}

Step ⌗10

Current Coordinate = {0.741, 7.33102}   Energy = -458.389

Eigenvalues = {3464.64, 0.00172117}   Gradient ={-0.000213463, -0.000982284}

Force Constants = {{3464.64, 0.000370467}, {0.000370467, 0.00172117}}

New Coordinate = {0.741, 7.90173}

Step ⌗11

Current Coordinate = {0.741, 7.90173}   Energy = -458.39

Eigenvalues = {3464.64, 0.000633068}   Gradient ={-0.0000779279, -0.000361454}

Force Constants = {{3464.64, 0.000136001}, {0.000136001, 0.000633068}}

New Coordinate = {0.741, 8.47269}

Step ⌗12

Current Coordinate = {0.741, 8.47269}   Energy = -458.39

Eigenvalues = {3464.64, 0.000232877}   Gradient ={-0.0000285861, -0.000132984}

Force Constants = {{3464.64, 0.0000499931}, {0.0000499931, 0.000232877}}

New Coordinate = {0.741, 9.04374}

Step ⌗13

Current Coordinate = {0.741, 9.04374}   Energy = -458.39

Eigenvalues = {3464.64, 0.0000856685}   Gradient ={-0.0000105051, -0.0000489238}

Force Constants = {{3464.64, 0.0000183862}, {0.0000183862, 0.0000856685}}

New Coordinate = {0.741, 9.61482}

Step ⌗14

Current Coordinate = {0.741, 9.61482}   Energy = -458.39

Eigenvalues = {3464.64, 0.0000315154}   Gradient ={-3.86311×10^{-6}, -0.0000179983}

Force Constants = {{3464.64, 6.76319×10^{-6}}, {6.76319×10^{-6}, 0.0000315154}}

New Coordinate = {0.741, 10.1859}

Optimization of Reactants

```
x0 = {4, 1.75};
AnalyticOptimize[x0, 15, 1 * 10^-5];
```

Optimization Process

Step ⌗1

Current Coordinate = {4., 1.75}   Energy = -293.673

Eigenvalues = {831.164, 0.117286}   Gradient ={-0.0623851, 184.615}

Force Constants = {{0.117287, 0.0319331}, {0.0319331, 831.164}}

New Coordinate = {4.59238, 1.52786}

Step ⌗2

Current Coordinate = {4.59238, 1.52786}   Energy = −301.269

Eigenvalues = {2846.02, 0.0430469}   Gradient ={−0.0226233, −190.098}

Force Constants = {{0.0430469, 0.0121318}, {0.0121318, 2846.02}}

New Coordinate = {5.09911, 1.59465}

Step ⌗3

Current Coordinate = {5.09911, 1.59465}   Energy = −308.266

Eigenvalues = {2038.35, 0.0158209}   Gradient ={−0.00835306, −28.1823}

Force Constants = {{0.0158209, 0.00425184}, {0.00425184, 2038.35}}

New Coordinate = {5.62337, 1.60848}

Step ⌗4

Current Coordinate = {5.62337, 1.60848}   Energy = −308.468

Eigenvalues = {1896.73, 0.00581123}   Gradient ={−0.00307742, −0.988934}

Force Constants = {{0.00581123, 0.00162386}, {0.00162386, 1896.73}}

New Coordinate = {6.15279, 1.609}

Step ⌗5

Current Coordinate = {6.15279, 1.609}   Energy = −308.469

Eigenvalues = {1891.55, 0.00213489}   Gradient ={−0.00113372, −0.00165207}

Force Constants = {{0.00213489, 0.000637336}, {0.000637336, 1891.55}}

New Coordinate = {6.68383, 1.609}

Step ⌗6

Current Coordinate = {6.68383, 1.609}   Energy = −308.47

Eigenvalues = {1891.54, 0.000784374}   Gradient ={−0.000417617, −0.000118384}

Force Constants = {{0.000784374, 0.000250876}, {0.000250876, 1891.54}}

New Coordinate = {7.21625, 1.609}

Step ⌗7

Current Coordinate = {7.21625, 1.609}   Energy = −308.47

Eigenvalues = {1891.54, 0.00028819}   Gradient ={−0.000153827, −0.0000467347}

Force Constants = {{0.00028819, 0.0000986776}, {0.0000986776, 1891.54}}

New Coordinate = {7.75002, 1.609}

Step ⌗8

Current Coordinate = {7.75002, 1.609}   Energy = −308.47

Eigenvalues = {1891.54, 0.000105884}   Gradient ={−0.0000566618, −0.0000184534}

Force Constants = {{0.000105884, 0.0000387429}, {0.0000387429, 1891.54}}

New Coordinate = {8.28515, 1.609}

Step ⌗9

Current Coordinate = {8.28515, 1.609}   Energy = −308.47

Eigenvalues = {1891.54, 0.000038902}   Gradient $=\{-0.0000208716, -7.27594\times10^{-6}\}$

Force Constants = {{0.000038902, 0.0000151779}, {0.0000151779, 1891.54}}

New Coordinate = {8.82167, 1.609}

```
hpp[{ri_, rj_, phi_}] = ∂phi,phi Ephi[{ri, rj, phi}];
r3[{ri_, rj_, phi_}] := (ri^2 + rj^2 - 2 * ri * rj * Cos[phi Degree]) ^ (1 / 2);
r1 = 1.790724790750559`;
r2 = 1.6163947202573365`;
xx = {r1, r2, 180}
r3[xx]
- (r1 * r2 / r3[xx]) * hpp[xx]
hpp[xx]
rkk = r3[{ri, rj, phi}];
hkk[{ri_, rj_, rk_}] = ∂rk,rk Eϕ[{ri, rj, rk}];
hkp[{ri_, rj_, phi_}] = hkk[{ri, rj, rkk}];
hkp[xx]
- (r1 * r2 / r3[xx]) * hkp[xx]
```

```
{1.79072, 1.61639, 180}
```

```
3.40712
```

```
-0.00145068
```

```
0.00170759
```

```
11.2024
```

```
-9.51703
```