```
In[453]:= (* Analytic KEO for a triatomic molecule using the valence bond coordinates *)

ClearAll["Global`*"]

natoms = 3;
ncoords = 3;
mass = {m1, m2, m3};
coords = {r1, r2, alpha};

(* Cartesian coords of atoms *)
cart = {
   {0, 0, 0},
   {r1 * Sin[alpha / 2], 0, r1 * Cos[alpha / 2]},
   {-r2 * Sin[alpha / 2], 0, r2 * Cos[alpha / 2]}
  };

Print["Cartesian coordinates"];
cart // MatrixForm

(* centre of mass *)
cm = {0, 0, 0};
For[ix = 1, ix ≤ 3, ix++,
 For[i = 1, i ≤ natoms, i++,
  cm[[ix]] = cm[[ix]] + cart[[i, ix]] * mass[[i]]
 ]]
For[ix = 1, ix ≤ 3, ix++,
 cm[[ix]] = cm[[ix]] / Total[mass]
]

(* Cartesian coords wrt centre of mass *)
For[ix = 1, ix ≤ 3, ix++,
 For[i = 1, i ≤ natoms, i++,
  cart[[i, ix]] = cart[[i, ix]] - cm[[ix]]
 ]]

Print["Cartesian coordinates wrt CM"];
cart = cart // Simplify;
cart // MatrixForm

(* t-vectors *)
tmat = ConstantArray[0, {natoms * 3, natoms * 3}];
```

```
xatom = 0;

For[x = 1, x ≤ 3, x++,
 For[atom = 1, atom ≤ natoms, atom++,
  xatom++;

  For[coord = 1, coord ≤ natoms * 3, coord++,

   If[coord ≤ ncoords,
    tmat[[xatom, coord]] = D[cart[[atom, x]], coords[[coord]]],
    If[coord ≤ ncoords + 3,
     For[y = 1, y ≤ 3, y++,
      tmat[[xatom, coord]] = tmat[[xatom, coord]] +
        Normal[LeviCivitaTensor[3]][[x, coord - ncoords, y]] * cart[[atom, y]]
     ],
     y = coord - (ncoords + 3);
     If[x == y, tmat[[xatom, coord]] = 1]
    ]
   ]
  ]
 ]]

Print["t-vectors"];
tmat = tmat // Simplify;
tmat // MatrixForm

(* g-small matrix *)
gsmall = ConstantArray[0, {natoms * 3, natoms * 3}];
For[icoord = 1, icoord ≤ natoms * 3, icoord++,
 For[jcoord = 1, jcoord ≤ natoms * 3, jcoord++,
  xatom = 0;
  For[x = 1, x ≤ 3, x++,
   For[atom = 1, atom ≤ natoms, atom++,
    xatom++;
    gsmall[[icoord, jcoord]] =
     gsmall[[icoord, jcoord]] + tmat[[xatom, icoord]] * tmat[[xatom, jcoord]] * mass[[atom]]
   ]]
 ]]
gsmall = gsmall // Simplify;
Print["g-small matrix"];
gsmall // MatrixForm

(* G-big matrix *)
```

```
Gbig = Inverse[gsmall] // Simplify;
Print["G-big matrix"];
Gbig // MatrixForm

(* Pseudopotential *)

DetG = Det[Gbig];
DetG2 = DetG^2;
dDetG = ConstantArray[0, {ncoords}];
For[coord = 1, coord ≤ ncoords, coord++,
   dDetG[[coord]] = D[DetG, coords[[coord]]]
  ];
pseudo1 = (dDetG.Gbig[[1 ;; ncoords, 1 ;; ncoords]].dDetG) / DetG2;

pseudo2 = 0;
For[coord = 1, coord ≤ ncoords, coord++,
  tmp = (Gbig[[coord, 1 ;; ncoords]].dDetG) / DetG;
  pseudo2 = pseudo2 - 4 * D[tmp, coords[[coord]]]
]
pseudo = (pseudo1 + pseudo2) / 32 // FullSimplify;
Print["Pseudopotential"];
pseudo

(* evaluate G and pseudopotential at a point *)
repl = {r1 → 1.3359007, r2 → 1.3359007, alpha → 92.265883 * Pi / 180.0,
    m1 → 31.97207070, m2 → 1.00782505, m3 -> 1.00782505};
Print["G-big at a point  ", repl]
Gbig /. repl // MatrixForm
Print["Pseudopotential at a point  ", repl]
pseudo /. repl // MatrixForm
```

Cartesian coordinates

Out[460]//MatrixForm=

$$\begin{pmatrix} 0 & 0 & 0 \\ r1\,\mathrm{Sin}\left[\frac{alpha}{2}\right] & 0 & r1\,\mathrm{Cos}\left[\frac{alpha}{2}\right] \\ -r2\,\mathrm{Sin}\left[\frac{alpha}{2}\right] & 0 & r2\,\mathrm{Cos}\left[\frac{alpha}{2}\right] \end{pmatrix}$$

Cartesian coordinates wrt CM

Out[467]//MatrixForm=

$$\begin{pmatrix} -\frac{(m2\,r1-m3\,r2)\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & 0 & -\frac{(m2\,r1+m3\,r2)\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} \\ \frac{(m1\,r1+m3\,(r1+r2))\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & 0 & \frac{(m1\,r1+m3\,(r1-r2))\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} \\ -\frac{(m1\,r2+m2\,(r1+r2))\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & 0 & \frac{(m1\,r2+m2\,(-r1+r2))\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} \end{pmatrix}$$

t-vectors

Out[473]//MatrixForm=

$$\begin{pmatrix} -\frac{m2\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & \frac{m3\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & -\frac{(m2\,r1-m3\,r2)\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{2\,(m1+m2+m3)} & 0 & -\frac{(m2\,r1+m3\,r2)}{m1+m2\text{-}} \\ \frac{(m1+m3)\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & \frac{m3\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & \frac{(m1\,r1+m3\,(r1+r2))\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{2\,(m1+m2+m3)} & 0 & \frac{(m1\,r1+m3\,(r1-r2}{m1+m2+} \\ -\frac{m2\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & -\frac{(m1+m2)\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & -\frac{(m1\,r2+m2\,(r1+r2))\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{2\,(m1+m2+m3)} & 0 & \frac{(m1\,r2+m2\,(-r1+r2}{m1+m2+} \\ 0 & 0 & 0 & \frac{(m2\,r1+m3\,r2)\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & 0 \\ 0 & 0 & 0 & -\frac{(m1\,r1+m3\,(r1-r2))\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & 0 \\ 0 & 0 & 0 & -\frac{(m1\,r2+m2\,(-r1+r2))\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & 0 \\ -\frac{m2\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & -\frac{m3\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & \frac{(m2\,r1+m3\,r2)\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{2\,(m1+m2+m3)} & 0 & \frac{(m2\,r1-m3\,r2)\,\text{S}}{m1+m2+} \\ \frac{(m1+m3)\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & -\frac{m3\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & -\frac{(m1\,r1+m3\,(r1-r2))\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{2\,(m1+m2+m3)} & 0 & -\frac{(m1\,r1+m3\,(r1+r}{m1+m2\text{-}} \\ -\frac{m2\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & \frac{(m1+m2)\,\text{Cos}\left[\frac{\text{alpha}}{2}\right]}{m1+m2+m3} & -\frac{(m1\,r2+m2\,(-r1+r2))\,\text{Sin}\left[\frac{\text{alpha}}{2}\right]}{2\,(m1+m2+m3)} & 0 & \frac{(m1\,r2+m2\,(r1+r2}{m1+m2+} \end{pmatrix}$$

g-small matrix

Out[478]//MatrixForm=

$$
\begin{pmatrix}
\frac{m2\,(m1+m3)}{m1+m2+m3} & -\frac{m2\,m3\,Cos[alpha]}{m1+m2+m3} & \frac{m2\,m3\,r2\,Sin[alpha]}{2\,(m1+m2+m3)} & \\
-\frac{m2\,m3\,Cos[alpha]}{m1+m2+m3} & \frac{(m1+m2)\,m3}{m1+m2+m3} & \frac{m2\,m3\,r1\,Sin[alpha]}{2\,(m1+m2+m3)} & \\
\frac{m2\,m3\,r2\,Sin[alpha]}{2\,(m1+m2+m3)} & \frac{m2\,m3\,r1\,Sin[alpha]}{2\,(m1+m2+m3)} & \frac{m2\,m3\,(r1^2+r2^2)+m1\,(m2\,r1^2+m3\,r2^2)+2\,m2\,m3\,r1\,r2\,Cos[alpha]}{4\,(m1+m2+m3)} & \\
0 & 0 & 0 & \frac{(m2\,m3\,(r1-r2)^2+m1\,(m\ldots}{m1\ldots} \\
-\frac{m2\,m3\,r2\,Sin[alpha]}{m1+m2+m3} & \frac{m2\,m3\,r1\,Sin[alpha]}{m1+m2+m3} & \frac{m2\,m3\,(r1^2-r2^2)+m1\,(m2\,r1^2-m3\,r2^2)}{2\,(m1+m2+m3)} & \\
0 & 0 & 0 & \frac{(m2\,m3\,(-r1^2+r2^2)+m1\,(-\ldots}{2\,(m1\ldots} \\
0 & 0 & 0 & \\
0 & 0 & 0 & \\
0 & 0 & 0 &
\end{pmatrix}
$$

G-big matrix

Out[481]//MatrixForm=

$$
\begin{pmatrix}
\frac{1}{m1}+\frac{1}{m2} & \frac{Cos[alpha]}{m1} & -\frac{Sin[alpha]}{m1\,r2} & 0 \\
\frac{Cos[alpha]}{m1} & \frac{1}{m1}+\frac{1}{m3} & -\frac{Sin[alpha]}{m1\,r1} & 0 \\
-\frac{Sin[alpha]}{m1\,r2} & -\frac{Sin[alpha]}{m1\,r1} & \frac{m2\,m3\,(r1^2+r2^2)+m1\,(m2\,r1^2+m3\,r2^2)-2\,m2\,m3\,r1\,r2\,Cos[alpha]}{m1\,m2\,m3\,r1^2\,r2^2} & 0 \\
0 & 0 & 0 & \frac{(m2\,m3\,(r1+r2)^2+m1\,(m2\,r1^2+m3\,r2^2))\,Se\ldots}{4\,m1\,m2\,m3\,r1^2\,r2^2} \\
\frac{Sin[alpha]}{2\,m1\,r2} & -\frac{Sin[alpha]}{2\,m1\,r1} & \frac{1}{2}\left(\frac{1}{m2\,r1^2}+\frac{\frac{1}{r1^2}-\frac{1}{r2^2}}{m1}-\frac{1}{m3\,r2^2}\right) & 0 \\
0 & 0 & 0 & \frac{(m2\,m3\,(r1^2-r2^2)+m1\,(m2\,r1^2-m3\,r2^2))\,Cs\ldots}{2\,m1\,m2\,m3\,r1^2\,r2^2} \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
$$

Pseudopotential

Out[491]=

$$
\frac{1}{16\,m1\,m2\,m3\,r1^2\,r2^2}\big(3\,m2\,m3\,r1\,r2\,Cos[alpha] + (m2\,(m1+m3)\,r1^2 + (m1+m2)\,m3\,r2^2)\,(-3 + Cos[2\,alpha]) + m2\,m3\,r1\,r2\,Cos[3\,alpha]\big)\,Csc[alpha]^2
$$

G-big at a point

{r1 → 1.3359, r2 → 1.3359, alpha → 1.61034, m1 → 31.9721, m2 → 1.00783, m3 → 1.00783}

Out[494]//MatrixForm=

$$\begin{pmatrix}
1.02351 & -0.0012366 & -0.0233946 & 0 & 0.0116973 & 0 & 0 & 0 & \\
-0.0012366 & 1.02351 & -0.0233946 & 0 & -0.0116973 & 0 & 0 & 0 & \\
-0.0233946 & -0.0233946 & 1.14842 & 0 & 0. & 0 & 0 & 0 & \\
0 & 0 & 0 & 0.615371 & 0 & 0. & 0 & 0 & \\
0.0116973 & -0.0116973 & 0. & 0 & 0.286411 & 0 & 0 & 0 & \\
0 & 0 & 0 & 0. & 0 & 0.534843 & 0 & 0 & \\
0 & 0 & 0 & 0 & 0 & 0 & 0.0294224 & 0 & \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0.0294224 & \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & (
\end{pmatrix}$$

Pseudopotential at a point

{r1 → 1.3359, r2 → 1.3359, alpha → 1.61034, m1 → 31.9721, m2 → 1.00783, m3 → 1.00783}

Out[496]//MatrixForm=

−0.286982