Simplifying the two-mode model for Sissors

31 Aug 12

GJMA

$$\mathcal{H}_g = \frac{\hat{P}^2}{2m} + h_g(\hat{Q})$$

$$h_g(Q) = \frac{p^2}{2m} + V_g(q, Q)$$

$$V_g(q, Q) = Z(Q) + q\,F(Q) + q^2 S(Q)$$

$$Z(Q) = Z_0 - fQ - 2K\left(\frac{Q}{\ell}\right)^2 + \frac{5}{3}K\left(\frac{Q}{\ell}\right)^4 \quad ✓$$

$$F(Q) = -\frac{4K}{\ell}\left(\frac{Q}{\ell}\right)^2 \quad ✓$$

$$S(Q) = \frac{m\omega^2}{2} + \frac{10K}{\ell^2}\left(\frac{Q}{\ell}\right)^2 \quad ✓$$

$$q^2 S + qF + Z = S\left(q^2 + q\frac{F}{S}\right) + Z = S\left(q + \frac{F}{2S}\right)^2 + Z - \frac{F^2}{4S}$$

$$\boxed{V_g(q, Q) = \frac{m\omega^2(Q)}{2}\left(q - q_g(Q)\right)^2 + v_g(Q)}$$

$$\frac{m\omega^2(Q)}{2} = S \qquad \omega(Q) = \sqrt{\frac{2S}{m}} = \sqrt{\omega^2 + \frac{20K}{m\ell^2}\left(\frac{Q}{\ell}\right)^2}$$

We use

$$\boxed{\boldsymbol{\omega(Q)} = \omega\left[1 + \frac{10K}{m\omega^2\ell^2}\left(\frac{Q}{\ell}\right)^2\right]} \, .$$

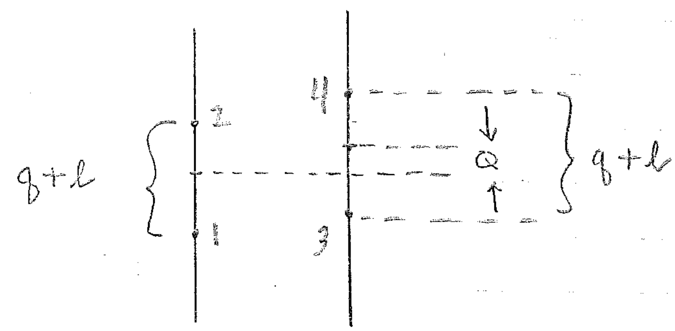
$$q_g(Q) = -\frac{F}{2S} = -\frac{-\frac{4K}{\ell}\left(\frac{Q}{\ell}\right)^2}{2\left(\frac{m\omega^2}{2} + \frac{10K}{\ell^2}\left(\frac{Q}{\ell}\right)^2\right)} \, .$$

We use $\boxed{\boldsymbol{q_g(Q)} = \frac{4K}{m\omega^2\ell}\left(\frac{Q}{\ell}\right)^2}$.

$v_g(Q) = Z - \frac{F^2}{4S}$; since $\frac{F^2}{4S} \propto K^2$, we use

$$\boxed{v_g(Q) = Z(Q)}$$

Our new version of $V_g(q,Q)$ agrees with the original through $O(K)$, as is verified on p. a



Two harmonically bound "atoms" of mass m constrained to move collinearly on each of two parallel lines. The bond lengths $q+l$ are equal but variable (viz. an antisymmetric vibrational mode is suppressed). The centers of mass of the two "molecules" are separated vertically by distance Q.

We see that

$$V_g(q, Q=0) = \frac{m\omega^2}{2} q^2 + Z_0 \, ,$$

so ω is the frequency of the symmetric vibrational mode at the $Q=0$ conformation.

The coupling constant K provides an attractive interaction between atoms 2 and 3 and atoms 1 and 4. It causes both of the equilibrium bond lengths $l + q_g(Q)$ as well as the vibrational frequency $\omega(Q)$ to increase when $Q \neq 0$. An "external field" $f > 0$ stabilizes conformations with positive Q relative to those with negative Q.

In the excited electronic state, the equilibrium bond lengths increase by δl at $Q = 0$. Accordingly

$$V_e(q, Q) = \frac{m\omega^2(Q)}{2}(q - q_e(Q))^2 + v_e(Q)$$

with

$$q_e(Q) = q_g(Q) + \delta l$$

and

$$v_e(Q) = v_g(Q) + \Delta v .$$

Let's find the extrema of the ground- and excited-state potentials. (4)

$$0 = \frac{\partial V_j(q, Q)}{\partial q} = m\omega^2(Q)(q - q_j(Q))$$

$$\Longrightarrow q = q_j(Q)$$

$$0 = \frac{\partial V_j(q, Q)}{\partial Q} = m\omega(Q)\frac{\partial \omega(Q)}{\partial Q}(q - q_j(Q))^2 - m\omega^2(Q)(q - q_j(Q))\frac{\partial q_j}{\partial Q} + \frac{\partial v_j(Q)}{\partial Q}$$

$$= \frac{\partial v_j(Q)}{\partial Q} = \frac{\partial v_g(Q)}{\partial Q} = \frac{\partial Z(Q)}{\partial Q}$$

$$0 = -f - \frac{4K}{\ell^2}Q + \frac{20K}{3\ell^4}Q^3$$

The solution – provided below for our chosen value of f – are the same for g- and e-states

Potential minima are at $(q, Q) = (q_g(Q_g), Q_g)$
and $(q, Q) = (q_e(Q_g), Q_g)$
$= (q_g(Q_g) + \delta\ell, Q_g)$.

We choose

$$\boxed{Z_0 = fQ_g + 2K\left(\frac{Q_g}{\ell}\right)^2 - \frac{5}{3}K\left(\frac{Q_g}{\ell}\right)^4}$$, so that $Z(Q_g) = 0$

and $V_g(q_g(Q_g), Q_g) = 0$. We choose

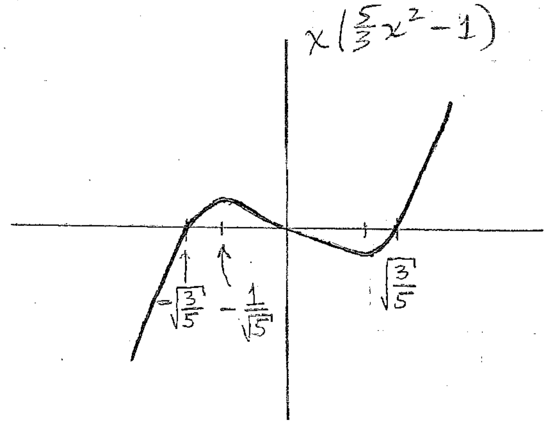
$\Delta U = \hbar\epsilon = V_e(q_e(Q_g), Q_g)$, so that

$\boxed{V_e(q_e(Q_g), Q_g) = \hbar\epsilon}$, and ϵ is the bare electronic transition frequency.

For an arbitrary external force, f, the solutions of $\partial V_j(q_j(Q), Q)/\partial Q = 0$ (common to $j = g$ & e) must be obtained numerically. Setting $x = Q/\ell$, this equation (p. 4) becomes

$$f = \frac{4K}{\ell} x\left(\frac{5}{3}x^2 - 1\right).$$

The RHS is sketched below:



For $f = 0$, the zeros of $x\left(\frac{5}{3}x^2 - 1\right)$ at $x = \pm\sqrt{\frac{3}{5}}$ correspond to potential minima, while that at $x = 0$ corresponds to a potential maximum ($V_j(q_j(Q), Q)$ is a symmetric double-well potential). The left minimum and the potential barrier move closer together with increasing f until, at (our chosen value) $\boldsymbol{f = \frac{8K}{\ell 3\sqrt{5}}}$, those two extrema coalesce to form an inflection point at $x = -1/\sqrt{5}$. In this case, the single potential well occurs at the remaining zero of $\frac{8K}{\ell 3\sqrt{5}} = \frac{4K}{\ell} x\left(\frac{5}{3}x^2 - 1\right)$, $x = 2/\sqrt{5}$ (or $\boldsymbol{Q_g = 2\ell/\sqrt{5}}$). In this case, we $\boldsymbol{Z_0 = \frac{8K}{5}}$ (p. 4).

In[1]:= `Clear["Global`*"]`

In[2]:= $\hbar = 1;$

In[3]:= $m = 1;$

In[4]:= $\omega = 2\pi;$

In[5]:= `(*Thus our unit of time is 2π/ω = 1.0*)`

In[6]:= `(*Our unit of length is*)`

$$N\left[\sqrt{\frac{\hbar}{2\,m\,\omega}}\right]$$

Out[6]= 0.282095

In[7]:= $l = 12\sqrt{\frac{\hbar}{2\,m\,\omega}};$

In[8]:= $\delta l = \sqrt{\frac{\hbar}{2\,m\,\omega}};$

In[9]:= $K = \frac{m\,\omega^2\,l^2}{432};$

In[10]:= $f = \frac{8}{3\sqrt{5}}\,\frac{K}{l};$

In[11]:= $\epsilon = 1000\,\omega;$

In[12]:= $Z0 = \frac{8\,K}{5};$

In[13]:= $Z[Q\_] := Z0 - f\,Q - 2\,K\left(\frac{Q}{l}\right)^2 + \frac{5}{3}\,K\left(\frac{Q}{l}\right)^4$

In[14]:= $F[Q\_] := -\frac{4\,K}{l}\left(\frac{Q}{l}\right)^2$

In[15]:= $S[Q\_] := \frac{m\,\omega^2}{2} + \frac{10\,K}{l^2}\left(\frac{Q}{l}\right)^2$

In[16]:= `(* We'll plot the various g-state functions *)`

In[17]:= $\text{omega}[Q\_] := \omega\left(1 + \frac{10\,K}{m\,\omega^2\,l^2}\left(\frac{Q}{l}\right)^2\right)$

In[18]:= $qg[Q\_] := \frac{4\,K}{m\,\omega^2\,l}\left(\frac{Q}{l}\right)^2$

In[19]:= $\upsilon g[Q\_] := Z[Q]$

In[20]:= $Vg[q\_, Q\_] := \frac{m\,(\text{omega}[Q])^2}{2}\,(q - qg[Q])^2 + \upsilon g[Q]$

In[21]:= `FindMinimum[Vg[qg[Q], Q], Q]`

Out[21]= {0., {Q → 3.02776}}

In[22]:= $2\,1 \big/ \sqrt{5.0}$

Out[22]= 3.02776

In[23]:= $\hbar\text{eg}[\text{n\_},\ \text{Q\_}] := \hbar\ \text{omega}[\text{Q}]\left(\text{n} + \frac{1}{2}\right) + \upsilon\text{g}[\text{Q}]$

In[24]:= `(* Now for the corresponding e-state functions *)`

In[25]:= $\text{qe}[\text{Q\_}] := \text{qg}[\text{Q}] + \delta 1$

In[26]:= $\upsilon\text{e}[\text{Q\_}] := \upsilon\text{g}[\text{Q}] + \hbar\,\epsilon$

In[27]:= $\text{Ve}[\text{q\_},\ \text{Q\_}] := \frac{\text{m}\ (\text{omega}[\text{Q}])^2}{2}\ (\text{q} - \text{qe}[\text{Q}])^2 + \upsilon\text{e}[\text{Q}]$

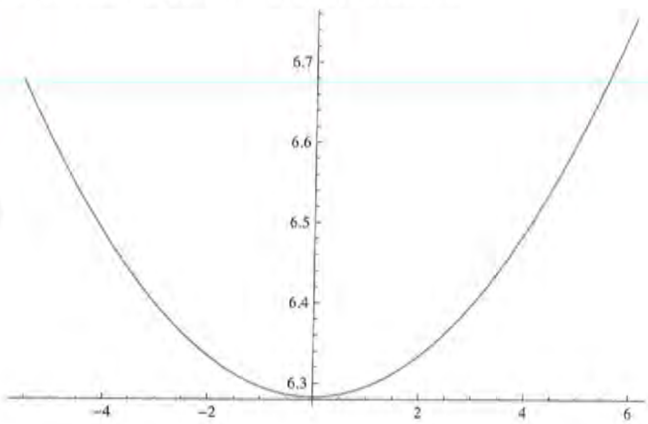
In[28]:= `FindMinimum[Ve[qe[Q], Q], {Q, 3}]`

Out[28]= {6283.19, {Q → 3.02776}}

In[29]:= $\hbar\text{ee}[\text{n\_},\ \text{Q\_}] := \hbar\ \text{omega}[\text{Q}]\left(\text{n} + \frac{1}{2}\right) + \upsilon\text{e}[\text{Q}]$

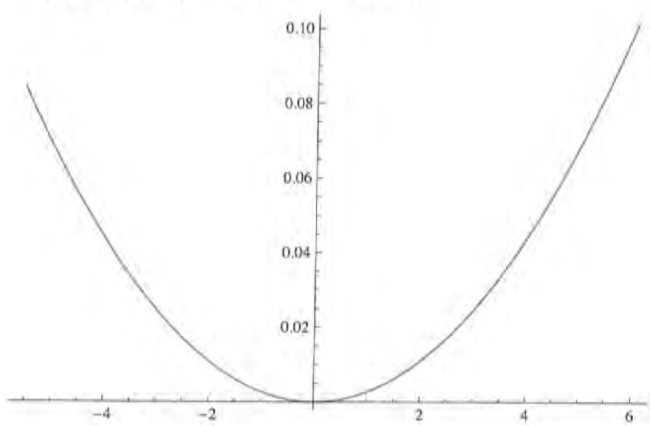
In[30]:= `Plot[omega[Q], {Q, -1.64 1, 1.80 1}]`

Out[30]=



In[31]:= `Plot[qg[Q], {Q, -1.64 1, 1.80 1}]`

Out[31]=



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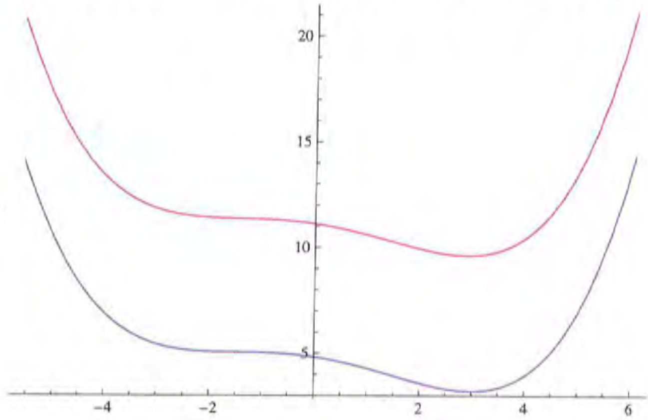
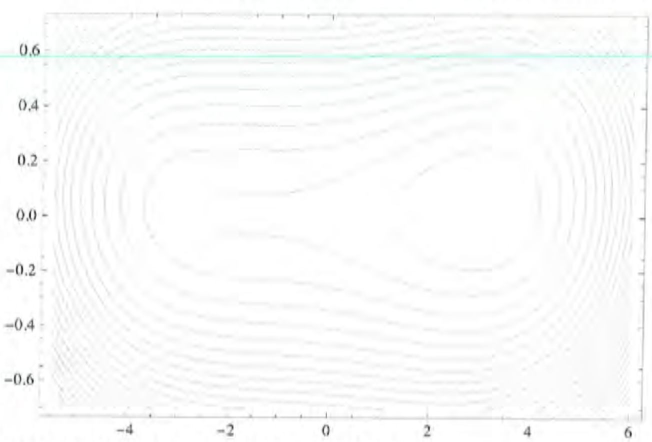
In[32]:= `Plot[{ħεg[0, Q], ħεg[1, Q]}, {Q, -1.64 l, 1.80 l}]`

Out[32]=



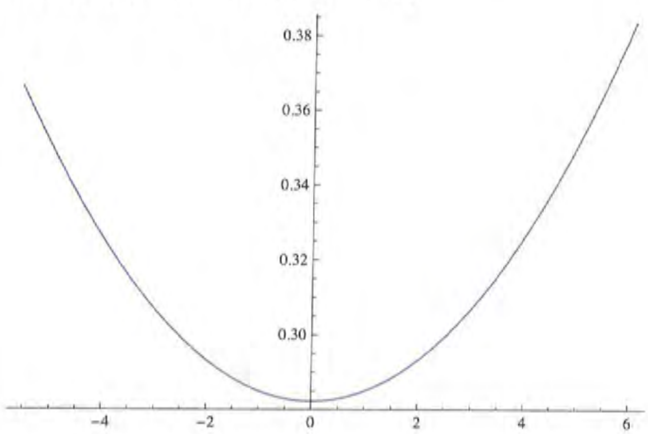
In[33]:= `ContourPlot`$\left[\texttt{Vg[q, Q]}, \{Q, -1.62\,l, 1.78\,l\}, \left\{q, -2.5\sqrt{\frac{\hbar}{2\,m\,\omega}}, 2.5\sqrt{\frac{\hbar}{2\,m\,\omega}}\right\},\right.$ `AspectRatio → 2 / 3, Contours → 24, ContourShading → None]`

Out[33]=



In[34]:= `Plot[qe[Q], {Q, -1.64 l, 1.80 l}]`

Out[34]=



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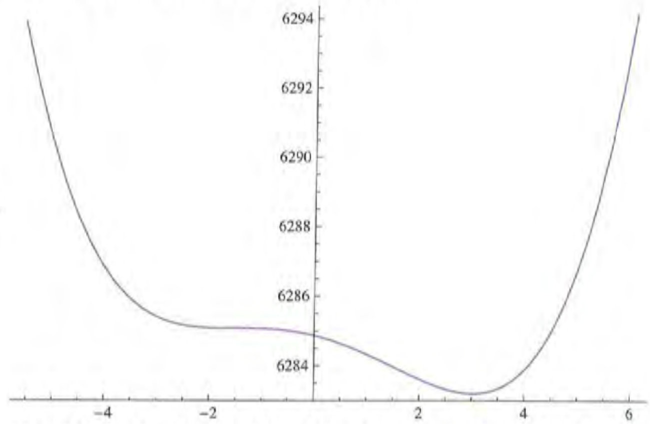
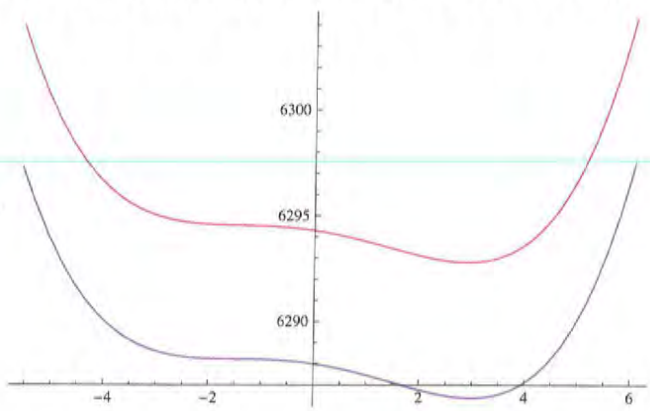
In[35]:= **Plot[υe[Q], {Q, -1.64 l, 1.80 l}]**

Out[35]=



In[36]:= **Plot[{ħee[0, Q], ħee[1, Q]}, {Q, -1.64 l, 1.80 l}]**

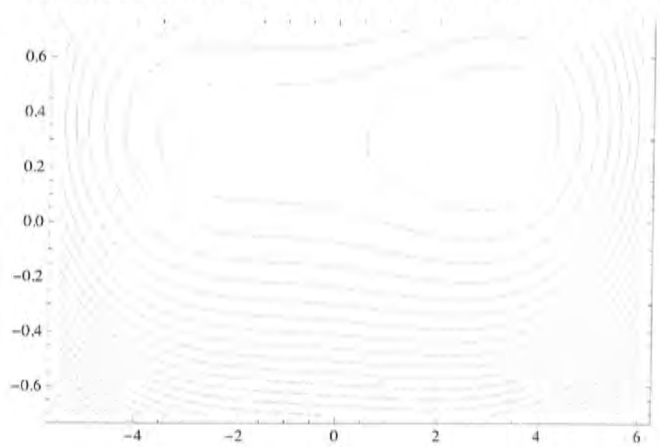
Out[36]=



In[37]:= **ContourPlot**$\left[\mathbf{Ve[q,\ Q]\ ,\ \{Q,\ -1.62\ l,\ 1.78\ l\},\ \left\{q,\ -2.5\sqrt{\frac{\hbar}{2\,m\,\omega}}\ ,\ 2.5\sqrt{\frac{\hbar}{2\,m\,\omega}}\right\},}\right.$

$\left.\mathbf{AspectRatio \to 2/3,\ Contours \to 24,\ ContourShading \to None}\right]$

Out[37]=



From pp. 1 and 2,

$$\frac{m\omega^2(Q)}{2}\left(q-q_g(Q)\right)^2+v_g(Q)$$

$$=\frac{m\omega^2}{2}\left[1+\frac{10K}{m\omega^2\ell^2}\left(\frac{Q}{\ell}\right)^2\right]^2\left[q-\frac{4K}{m\omega^2\ell}\left(\frac{Q}{\ell}\right)^2\right]^2+Z(Q)$$

$$=\frac{m\omega^2}{2}\left[1+\frac{20K}{m\omega^2\ell^2}\left(\frac{Q}{\ell}\right)^2+\frac{100K^2}{m^2\omega^4\ell^4}\left(\frac{Q}{\ell}\right)^4\right]\left[q^2-q\frac{8K}{m\omega^2\ell}\left(\frac{Q}{\ell}\right)^2\right.$$

$$\left.+\frac{16K^2}{m^2\omega^4\ell^2}\left(\frac{Q}{\ell}\right)^4\right]+Z(Q)$$

$$=q^2\left[\frac{m\omega^2}{2}+\frac{10K}{\ell^2}\left(\frac{Q}{\ell}\right)^2+\frac{50K^2}{m\omega^2\ell^4}\left(\frac{Q}{\ell}\right)^4\right]$$

$$+q\left[-\frac{4K}{\ell}\left(\frac{Q}{\ell}\right)^2-\frac{80K^2}{m\omega^2\ell^3}\left(\frac{Q}{\ell}\right)^4-\frac{400K^3}{m^2\omega^4\ell^5}\left(\frac{Q}{\ell}\right)^6\right]$$

$$+\frac{m\omega^2}{2}\left[1+\frac{20K}{m\omega^2\ell^2}\left(\frac{Q}{\ell}\right)^2+\frac{100K^2}{m^2\omega^4\ell^4}\left(\frac{Q}{\ell}\right)^4\right]\frac{16K^2}{m^2\omega^4\ell^2}\left(\frac{Q}{\ell}\right)^4$$

$$+Z(Q),$$

which agrees with the original expression for $V_g(q,Q)$ through first order in K.