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Variational Calculation of the Hydrogen Molecular Cation using Maple (II). The pi and pi-star Orbitals

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Variational Calculation of the Hydrogen Molecular Cation (H_2^+) using Maple (II). The π and π^* Orbitals

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I. SYNOPSIS

It is of interest to carry out a full calculation of the H_2^+ quantum mechanical energy as a function of the internuclear distance so that one understands that the 2-electron problem's difficulties are, at least partially, due to the electron-electron repulsion. We've done this already once with the ground state, but it seems worthwhile to look at π orbitals also, hence this reading.

II. INTRODUCTION

The p orbitals which combine to form π orbitals should be chosen from the set p_x and p_y, since the p_z orbitals are aligned along the z-axis, and therefore are cylindrically symmetric, and therefore combine to form σ orbitals, specicially p_σ and p_{σ^*}.

In our previous reading, http://digitalcommons.uconn.edu/chem_educ/36, we've given the coördinate transformations so, here we write

$$\psi_{LCAO-MO} = p_x^A + p_x^B = xe^{-\alpha r_A} + xe^{-\alpha r_B}$$

in mixed notation (we put the protons arbitrarily at point A (0,0,R/2) and B (0,0,-R/2)).

$$r_A = \frac{R}{2}(\lambda + \mu)$$

and

$$r_B = \frac{R}{2}(\lambda - \mu)$$

while

$$x = \frac{R}{2}\cos\phi\sqrt{(\lambda^2-1)(1-\mu^2)}$$

and

$$y = \frac{R}{2}\sin\phi\sqrt{(\lambda^2-1)(1-\mu^2)}$$

so

$$\psi_{LCAO-MO} = \frac{R}{2}\cos\phi\sqrt{(\lambda^2-1)(1-\mu^2)}e^{-\alpha r_A} + \frac{R}{2}\cos\phi\sqrt{(\lambda^2-1)(1-\mu^2)}e^{-\alpha r_B} \quad (2.1)$$

which is, finally

$$\psi_{LCAO-MO} = \frac{R}{2}\cos\phi\sqrt{(\lambda^2-1)(1-\mu^2)}e^{-\alpha\frac{R}{2}(\lambda+\mu)} + \frac{R}{2}\cos\phi\sqrt{(\lambda^2-1)(1-\mu^2)}e^{-\alpha\frac{R}{2}(\lambda-\mu)}$$

From this definition (of the π, and with a minus sign, the π^*) we can continue, using essentially the same code as before.

```
> restart;
> with(plots):
> with(plottools);
> assume(k>0,R>0);
> psi_A :=
> (R/2)*cos(phi)*sqrt((lambda^2-1)*(1-mu^2))*exp(-k*(R/2)*(lambda-mu)/2)
> ;
> psi_B :=
> (R/2)*cos(phi)*sqrt((lambda^2-1)*(1-mu^2))*exp(-k*(R/2)*(lambda+mu)/2)
> ;
> r_A := (R/2)*(lambda-mu);
> r_B := (R/2)*(lambda+mu);
> dtau := ((R^3)/8)*(lambda^2-mu^2);


> #================================================
> t1 := (psi_A**2)*2*Pi*((R**3)/8)*(lambda**2-mu**2):
> t2 := expand(int(t1,mu=-1..1)):
> t2 := collect(t2,exp(k*R*lambda)):
> SAA := int(t2,lambda=1..infinity):
> psi_A := psi_A/sqrt(SAA):#normalize
```

```
> t11 := (psi_B**2)*2*Pi*((R**3)/8)*(lambda**2-mu**2):
> t21 := expand(int(t11,mu=-1..1)):
> t21 := collect(t21,exp(k*R*lambda)):
> SBB := int(t21,lambda=1..infinity):
> psi_B := psi_B/sqrt(SBB):
> t3 := 2*Pi*psi_A*psi_B*((R**3)/8)*(lambda**2-mu**2):
> t4 := expand(int(t3,mu=-1..1)):
> t4 := collect(t4,exp(k*R*lambda)):
> SAB := expand(int(t4,lambda=1..infinity)):
> SAB := collect(SAB,exp(k*R)):
> #start HAA section:
> t5 := 4/((R**2)*(lambda**2-mu**2))*
> (diff((lambda**2-1)*diff(psi_A,lambda),lambda)+
> diff((1-mu**2)*diff(psi_A,mu),mu)):
> t6 :=psi_A* 2*Pi*((-hbar**2)/(2*m))*t5*dtau
> -2*Pi*Z_A*esq*(1/r_A)*psi_A*psi_A*dtau
> -2*Pi*Z_A*esq*(1/r_B)*psi_A*psi_A*dtau:
> HAA := int(t6,mu=-1..1):
> HAA := int(HAA,lambda=1..infinity):
> #HAB section
> t5B := 4/((R**2)*(lambda**2-mu**2))*
> (diff((lambda**2-1)*diff(psi_B,lambda),lambda)+
> diff((1-mu**2)*diff(psi_B,mu),mu)):
> t61 :=psi_A* 2*Pi*((-hbar**2)/(2*m))*t5B*dtau
> -2*Pi*Z_A*esq*(1/r_A)*psi_B*psi_A*dtau
> -2*Pi*Z_A*esq*(1/r_B)*psi_B*psi_A*dtau:
> HAB := int(t61,mu=-1..1):
> HAB := collect(HAB,exp(k*R)):
> HAB := int(HAB,lambda=1..infinity):
> HAB := collect(HAB,exp(k*R)):
> Energy_one := (HAA-HAB)/(1-SAB):
> Energy_two := (HAB + HAA)/(SAB+1):
> #specialize to homonuclear Z=1 case
> Energy_one := subs(Z_A=1,Z_B=1,Energy_one):
> Energy_two := subs(Z_A=1,Z_B=1,Energy_two):
> Energy_one := subs(esq=1,hbar=1,m=1,Energy_one):
> Energy_two := subs(esq=1,hbar=1,m=1,Energy_two):
```

$$Energy\_one := \frac{-\frac{1}{6}\frac{e^{(-k\tilde{}\,R\tilde{})}\,\pi\,(-3+k\tilde{}^{2}\,R\tilde{}^{2}-3\,k\tilde{}\,R\tilde{})}{k\tilde{}}-\frac{1}{2}\,\frac{\pi}{k\tilde{}}}{\frac{\frac{1}{3}\,\frac{\pi\,R\tilde{}^{2}}{k\tilde{}}+\frac{\pi\,R\tilde{}}{k\tilde{}^{2}}+\frac{\pi}{k\tilde{}^{3}}}{e^{(k\tilde{}\,R\tilde{})}}-\frac{\pi}{k\tilde{}^{3}}}$$

```
> plot3d({Energy_one+1/R,Energy_two+1/R
> },k=2.0..3.5,R=1.2..6,axes=BOXED);

> En5 := subs(R=2.0,Energy_two+1/R):
> En6 := subs(R=2.2,Energy_two+1/R):
> En7 := subs(R=2.4,Energy_two+1/R):
> En8 := subs(R=2.6,Energy_two+1/R):
> En9 := subs(R=2.8,Energy_two+1/R):
> En10 := subs(R=3.0,Energy_two+1/R):
> En11 := subs(R=3.2,Energy_two+1/R):
> En12 := subs(R=3.4,Energy_two+1/R):
> En13 := subs(R=3.6,Energy_two+1/R):
> En14 := subs(R=3.8,Energy_two+1/R):
> En15 := subs(R=4.0,Energy_two+1/R):
> plot({En5,En6,En7,En8,En9,En10,En11,En12,En13,En14,En15
> },k=2.0..4.0,labels=[`k`,`Energy`],title=`Variation of Exponential
> k`);
> contourplot(Energy_two+1/R,R=0.8..8,k=1..4.0,contours = 80);
> #choose 2.3 (by eye);

Warning, the name changecoords has been redefined

Warning, the name arrow has been redefined
```

[*arc*, *arrow*, *circle*, *cone*, *cuboid*, *curve*, *cutin*, *cutout*, *cylinder*, *disk*, *dodecahedron*, *ellipse*, *ellipticArc*, *hemisphere*, *hexahedron*, *homothety*, *hyperbola*, *icosahedron*, *line*, *octahedron*, *pieslice*, *point*, *polygon*, *project*, *rectangle*, *reflect*, *rotate*, *scale*, *semitorus*, *sphere*, *stellate*, *tetrahedron*, *torus*, *transform*, *translate*, *vrml*]

$$psi\_A := \frac{1}{2} R\tilde{} \cos(\phi) \sqrt{(\lambda^2 - 1)(1 - \mu^2)}\, e^{(-\frac{k\tilde{} R\tilde{} (\lambda - \mu)}{4})}$$

$$psi\_B := \frac{1}{2} R\tilde{} \cos(\phi) \sqrt{(\lambda^2 - 1)(1 - \mu^2)}\, e^{(-\frac{k\tilde{} R\tilde{} (\lambda + \mu)}{4})}$$

$$r\_A := \frac{R\tilde{} (\lambda - \mu)}{2}$$

$$r\_B := \frac{R\tilde{} (\lambda + \mu)}{2}$$

$$dtau := \frac{R\tilde{}^3 (\lambda^2 - \mu^2)}{8}$$

```
> x_limit := 8;
> limit1 := limit(subs(k=2.3,Energy_one+1/R),R=infinity);
> limit2 := limit(subs(k=2.3,Energy_two+1/R),R=infinity);
> line1 := line([4.6,-0.2443749999], [x_limit,-0.2443749999], color=red,
> linestyle=3):
> line2 := line([4.6,-0.2443749999], [3.8,-0.28], color=blue,
> linestyle=3):
> line3 := line([4.6,-0.2443749999], [3.8,-0.1], color=green,
> linestyle=3):
> line4 := line([3.8,-0.28], [2.8,-0.28], color=blue, linestyle=3):
> line5 := line([3.8,-0.1], [2.8,-0.1], color=green, linestyle=3):
> larrow := arrow([3.4,-0.28], [3.4,-0.1], .2, .4, .1, color=green):
> myplot := plot({subs(k=2.3,Energy_two+1/R),
> subs(k=2.3,Energy_one+1/R)
> },R=1..8.0,labels=[`R`,`Energy(R)`],title=`E(R)`):
> display({myplot,line1,line2,line3,line4,line5,larrow});
```

$$x\_limit := 8$$

$$limit1 := -0.2443749999$$

$$limit2 := -0.2443749999$$

III. FIGURES

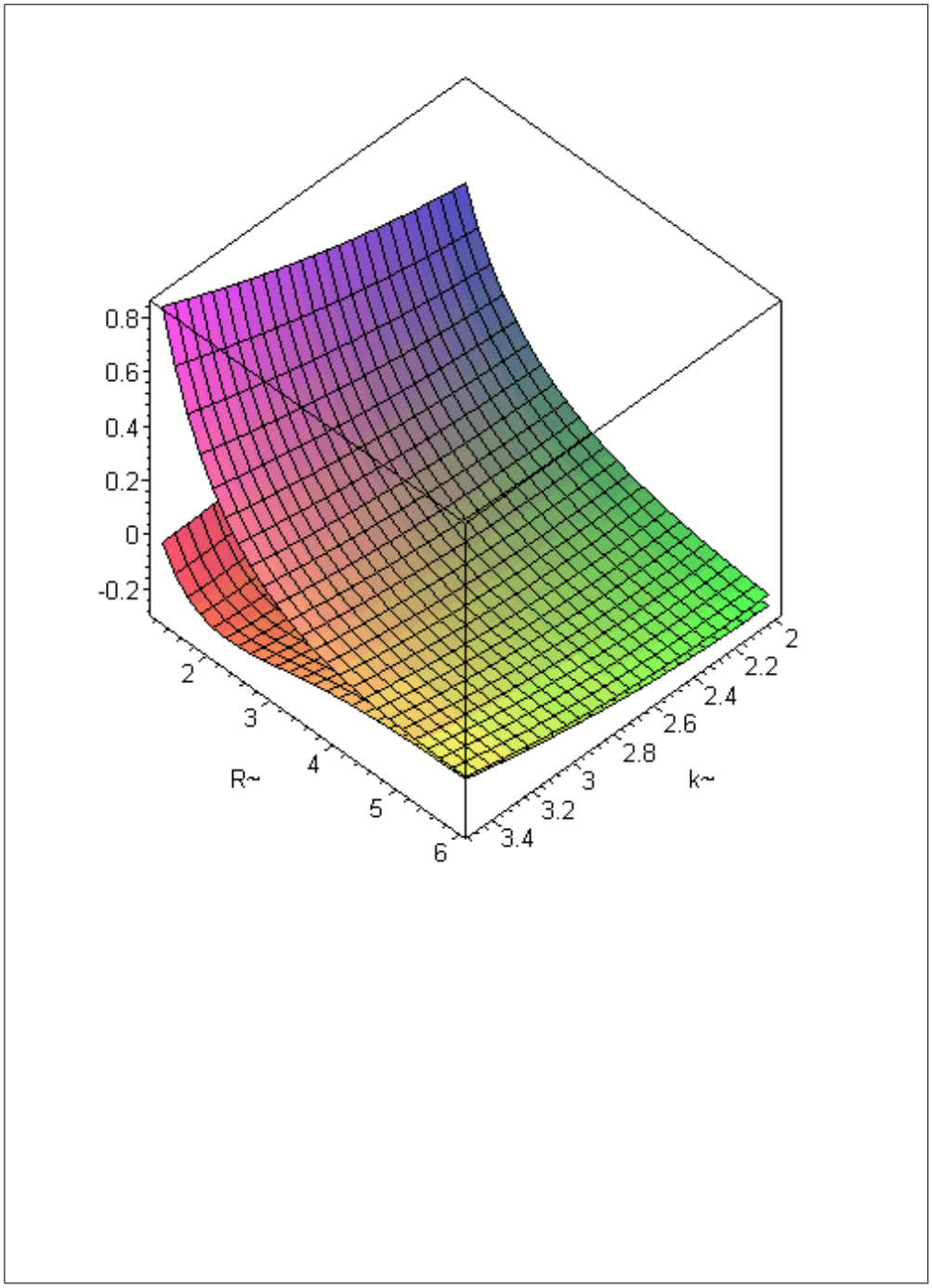

FIG. 1: Energies of the ground and first excited states of the electron of the H_2^+ cation

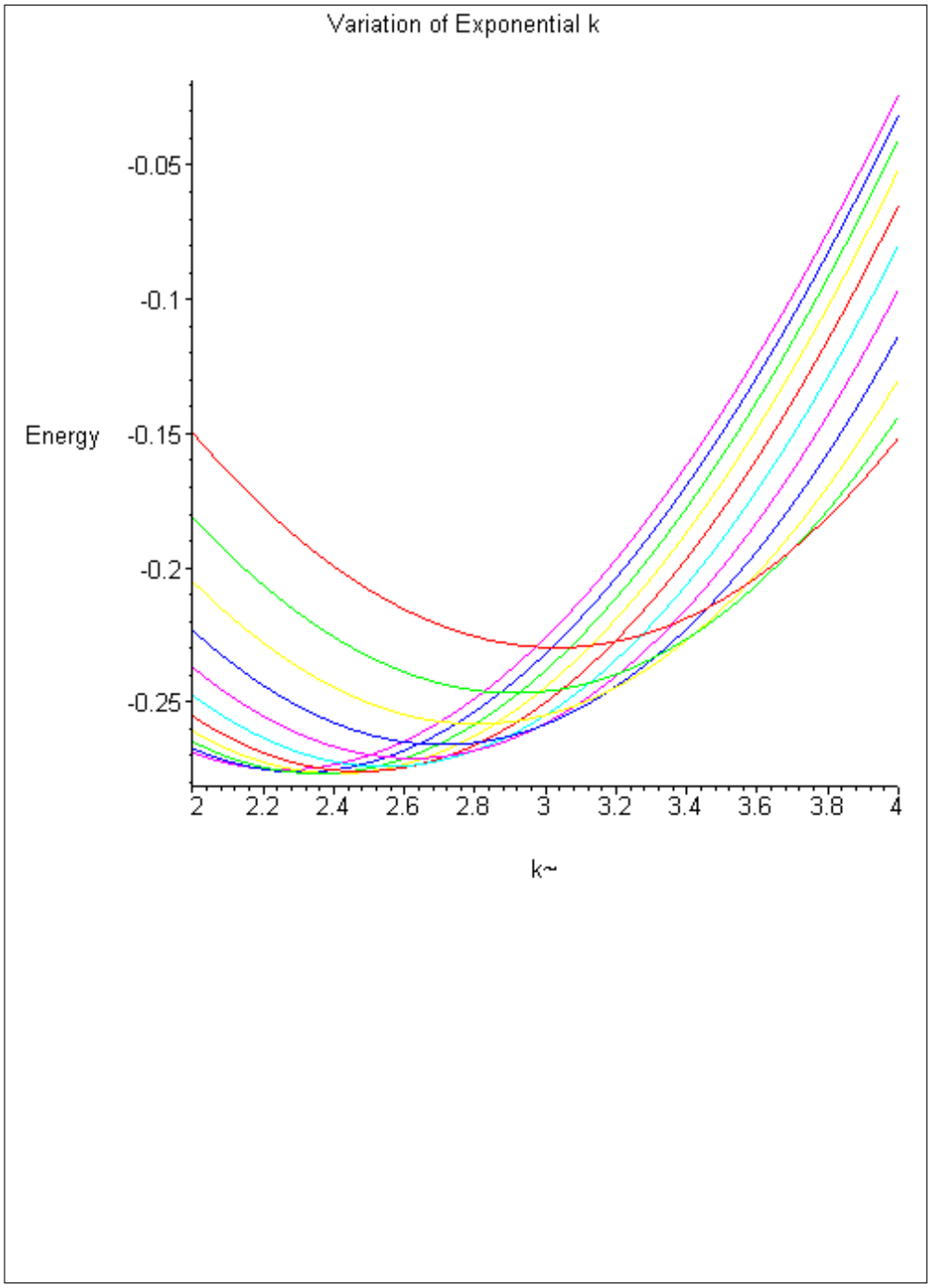

FIG. 2: WRONG Energies of the ground and first excited states of the electron of the H_2^+ cation assuming a fixed value of k=2.3, plotted as a function or the internuclear distance R

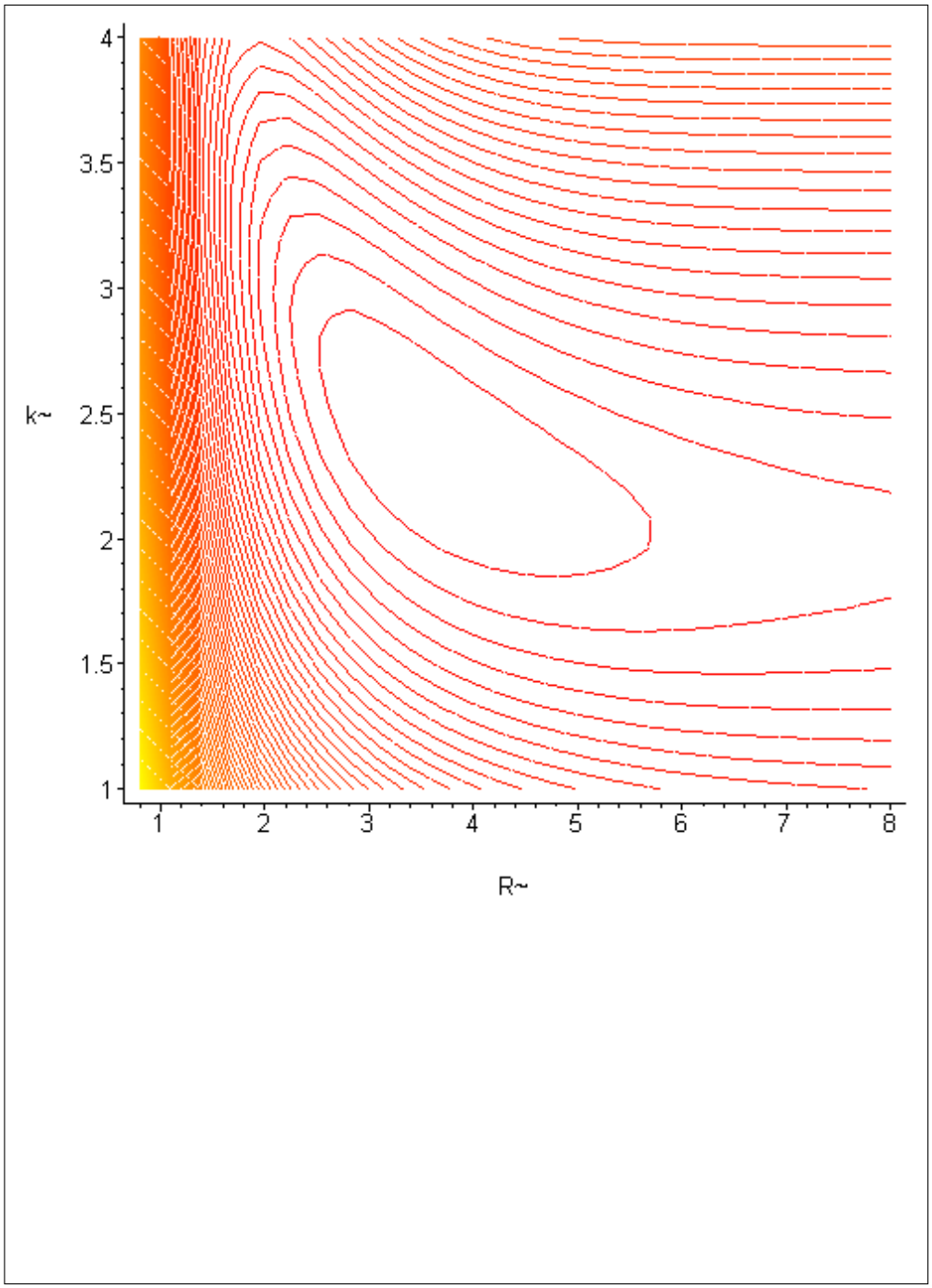

FIG. 3: Contours of the Energy as a function of R and k

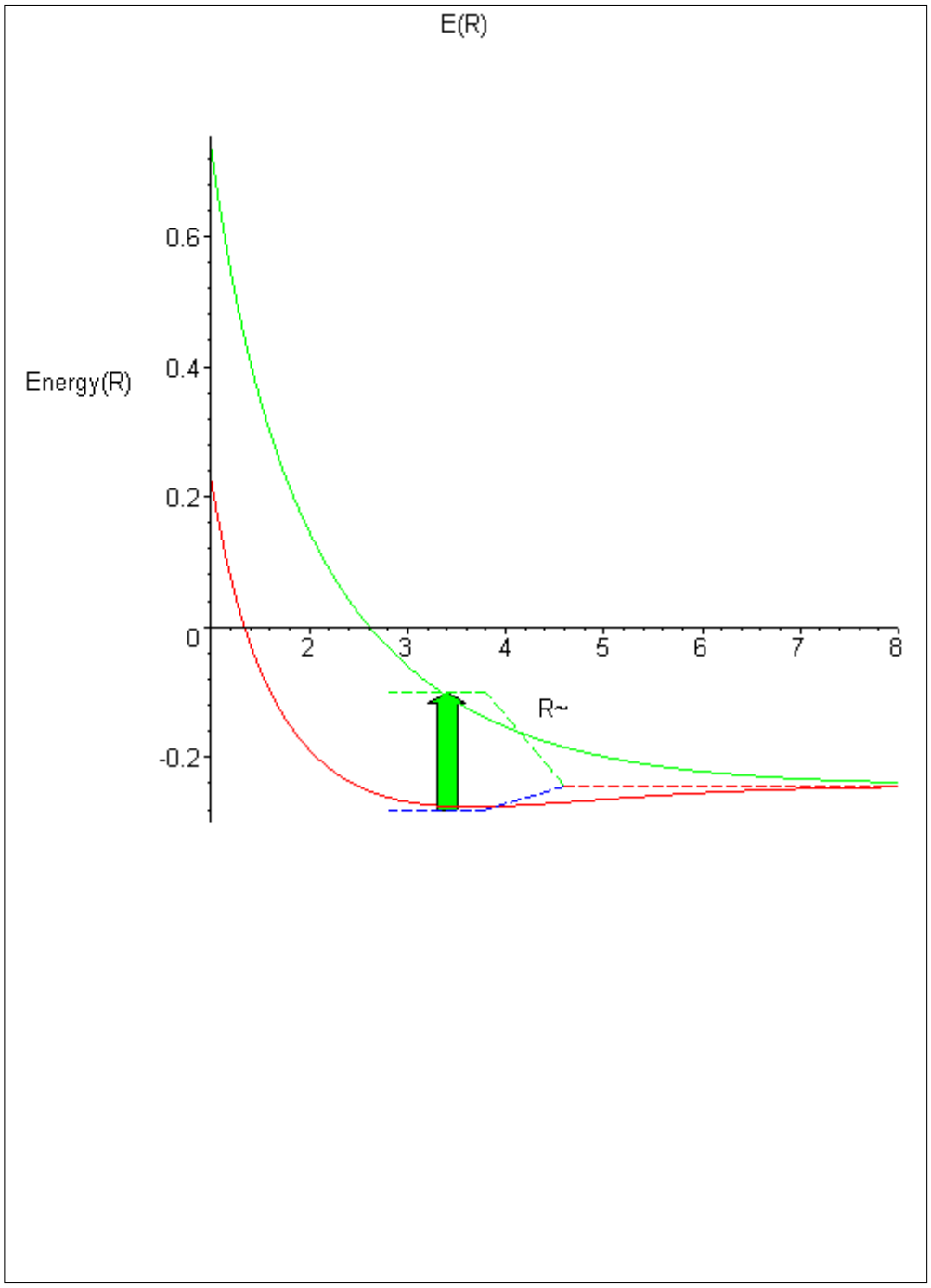

FIG. 4: Energy as a function of R and k (π and π^*)