Homework 1 **John Waczak**
PH 653 Date: May 7, 2019
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1 Consider hydrogen atom. Apply the variational method and calculate an approximate value for the energy of the ground state using the following trial functions:

$$\begin{aligned}
&(a) \qquad \psi_a = e^{-ar}, \qquad a > 0\\
&(b) \qquad \psi_a = re^{-ar}, \qquad a > 0\\
&(c) \qquad \psi_a = \frac{r}{r^2+a^2}\\
&(d) \qquad \psi_a = \frac{1}{r^2+a^2}
\end{aligned}$$

In each case, compare the approximate result to the energy values obtained via exact calculation. Which trial function yields the energy value which agrees the best with the exact value?

To estimate the energy of the ground state, we must minimize the expectation value of the Hamiltonian with respect to the parameter a for a test function ψ_a, i.e.

$$\left\langle \hat{H} \right\rangle (a) = \frac{\left\langle \psi_a \middle| \hat{H} \middle| \psi_a \right\rangle}{\langle \psi_a | \psi_a \rangle} \tag{1}$$

It is best if we start with the normalization factor $\langle \psi_a | \psi_a \rangle$ as this will allow us to check if ψ_a is reasonable before continuing with the harder $\left\langle \psi_a \middle| \hat{H} \middle| \psi_a \right\rangle$ calculation.

$$\langle \psi_a | \psi_a \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin\theta \; dr d\theta d\phi \, |\psi_a(r)|^2 \tag{2}$$

$$\tag{3}$$

Recalling the useful integral identity

$$\int_0^\infty x^n e^{-\alpha x} dx = \frac{\Gamma(n+1)}{\alpha^{n+1}} \tag{4}$$

enables us to solve the integrals.

Having chosen a reasonably behaved test function we may continue with the calculation. We now must calculate the matrix element $\left\langle \psi_a \middle| \hat{H} \middle| \psi_a \right\rangle$. For the hydrogen atom, our Hamiltonian is given by

$$\begin{aligned}
\hat{H} &= -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{q^2}{r} && (5)\\
&= -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{1}{4\pi\epsilon_0}\frac{q^2}{r} && (6)
\end{aligned}$$

where the final line follows as ψ_a only has r dependence. With this, the matrix element becomes

$$\left\langle \psi_a \middle| \hat{H} \middle| \psi_a \right\rangle = 4\pi \int_0^\infty \psi_a \left[\hat{H}\ \psi_a \right] r^2 dr \tag{7}$$

To save time, I've calculated the value of these two integrals for each test function in the following Mathematica notebook.

Define test functions

In[151]:=
```
$Assumptions = a > 0
ψ1 = Exp[-a * r]
ψ2 = r * Exp[-a * r]
```
$\psi_3 = \dfrac{r}{r\hat{}2 + a\hat{}2}$

$\psi_4 = \dfrac{1}{r\hat{}2 + a\hat{}2}$

Out[151]= $a > 0$

Out[152]= $e^{-a r}$

Out[153]= $e^{-a r}\, r$

Calculate normalization coefficient

In[154]:=
```
N1 = Integrate[4 * π * r^2 * ψ1^2, {r, 0, ∞}]
N2 = Integrate[4 * π * r^2 * ψ2^2, {r, 0, ∞}]
N3 = Integrate[4 * π * r^2 * ψ3^2, {r, 0, ∞}]
N4 = Integrate[4 * π * r^2 * ψ4^2, {r, 0, ∞}]
```

Out[154]= $\frac{\pi}{a^3}$

Out[155]= $\frac{3\,\pi}{a^5}$

... Integrate: Integral of $4\,\pi\,r^2\,\psi_3^2$ does not converge on $\{0, \infty\}$.

... Integrate: Integral of $4\,\pi\,r^2\,\psi_3^2$ does not converge on $\{0, \infty\}$.

Out[156]= $\int_0^\infty 4\,\pi\,r^2\,\psi_3^2\,dr$

Out[157]= $\frac{\pi^2}{a}$

Clearly the ψ_3 won’t work as a test function because we can’t normalize it.

Define Laplacian and Hamiltonian operators

In[158]:=

$\text{lap}[\psi\_, r\_] := \dfrac{1}{r\hat{}2} D[(r\hat{}2 * D[\psi, r]), r]$

$H[\psi\_,\ r\_] := \dfrac{-h\hat{}2}{2\,\mu} * \text{lap}[\psi, r] - \dfrac{q\hat{}2}{4 * \pi * \epsilon * r} * \psi$

Calculate Hamiltonains

In[160]:=
```
Hψ₁ = H[ψ₁, r]
Hψ₂ = H[ψ₂, r]
Hψ₄ = H[ψ₄, r]
```

Out[160]= $-\frac{e^{-a r} q^2}{4 \pi r \epsilon} - \frac{h^2 \left(-2 a e^{-a r} r + a^2 e^{-a r} r^2\right)}{2 r^2 \mu}$

Out[161]= $-\frac{e^{-a r} q^2}{4 \pi \epsilon} - \frac{h^2 \left(2 r \left(e^{-a r} - a e^{-a r} r\right) + r^2 \left(-2 a e^{-a r} + a^2 e^{-a r} r\right)\right)}{2 r^2 \mu}$

Out[162]= $-\frac{q^2}{4 \pi r \left(a^2 + r^2\right) \epsilon} - \frac{h^2 \left(\frac{8 r^4}{\left(a^2+r^2\right)^3} - \frac{6 r^2}{\left(a^2+r^2\right)^2}\right)}{2 r^2 \mu}$

Integrate against $4\pi r^2$

In[163]:=
```
I₁ = Integrate[4 π * r^2 * ψ₁ * Hψ₁ , {r, 0, ∞}]
```

Out[163]= $\frac{2 a h^2 \pi \epsilon - q^2 \mu}{4 a^2 \epsilon \mu}$

In[164]:=
```
I₂ = Integrate[4 π * r^2 * ψ₂ * Hψ₂, {r, 0, ∞}]
```

Out[164]= $\frac{4 a h^2 \pi \epsilon - 3 q^2 \mu}{8 a^4 \epsilon \mu}$

In[165]:=
```
I₄ = Integrate[4 π * r^2 * ψ₄ * Hψ₄, {r, 0, ∞}]
```

Out[165]= $\frac{h^2 \pi^2 \epsilon - 2 a q^2 \mu}{4 a^3 \epsilon \mu}$

Solve for the expectation value

In[166]:=
```
Expec₁ = I₁ / N₁
Expec₂ = I₂ / N₂
Expec₄ = I₄ / N₄
```

Out[166]= $\frac{a \left(2 a h^2 \pi \epsilon - q^2 \mu\right)}{4 \pi \epsilon \mu}$

Out[167]= $\frac{a \left(4 a h^2 \pi \epsilon - 3 q^2 \mu\right)}{24 \pi \epsilon \mu}$

Out[168]= $\frac{h^2 \pi^2 \epsilon - 2 a q^2 \mu}{4 a^2 \pi^2 \epsilon \mu}$

In summary we found that $\psi_a = \frac{r}{r^2+a^2}$ is not a suitable test function and that for the other three functions, the parametrized expectation value is

$$(a) \qquad \langle \hat{H} \rangle (a) = \frac{a^2 h^2}{2\mu} - \frac{a q^2}{4\pi\epsilon_0} \tag{8}$$

$$(b) \qquad \langle \hat{H} \rangle (a) = \frac{a^2 \hbar^2}{6\mu} - \frac{a q^2}{8\pi\epsilon_0} \tag{9}$$

$$(d) \qquad \langle \hat{H} \rangle (a) = \frac{\hbar^2}{4a^2\mu} - \frac{q^2}{2a\pi^2\epsilon_0} \tag{10}$$

Now we can take the derivative of these equations w.r.t. a in order to minimize for the ground state energy estimate.

$$(a) \qquad \frac{\partial}{\partial a} \langle \hat{H} \rangle (a) = \frac{a\hbar^2}{\mu} - \frac{q^2}{4\pi\epsilon_0} \tag{11}$$

$$(b) \qquad \frac{\partial}{\partial a} \langle \hat{H} \rangle (a) = \frac{a\hbar^2}{3\mu} - \frac{q^2}{8\pi\epsilon_0} \tag{12}$$

$$(d) \qquad \frac{\partial}{\partial a} \langle \hat{H} \rangle (a) = -\frac{\hbar^2}{2a^3\mu} + \frac{q^2}{2a^2\pi^2\epsilon_0} \tag{13}$$

Setting each of these equations equal to zero and solving for a yields

$$(a) \qquad a = \frac{q^2\mu}{4\hbar^2\pi\epsilon_0} \tag{14}$$

$$(b) \qquad a = \frac{3q^2\mu}{8\hbar^2\pi\epsilon_0} \tag{15}$$

$$(d) \qquad a = \frac{\hbar^2\pi^2\epsilon_0}{q^2\mu} \tag{16}$$

Finally, re-substituting into previous set of equations gives the ground state energy estimates for each test function.

$$(a) \qquad E_{gs} \approx -\frac{q^4\mu}{32\hbar^2\pi^2\epsilon_0^2} \tag{17}$$

$$(b) \qquad E_{gs} \approx -\frac{3q^4\mu}{128\hbar^2\pi^2\varepsilon_0^2} \tag{18}$$

$$(d) \qquad E_{gs} \approx -\frac{q^4\mu}{4\hbar^2\pi^4\epsilon_0^2} \tag{19}$$

For the real value, recall from last term that the energy levels of the unperturbed hydrogen atom are given by

$$E_n = -\frac{1}{2n^2}\left(\frac{q^2}{4\pi\epsilon_0}\right)^2 \frac{\mu}{\hbar^2} \tag{20}$$

so that the ground state energy level is exactly

$$E_{gs} = -\frac{q^4\mu}{32\pi^2\epsilon_0^2\hbar^2} \tag{21}$$

Therefore, we see that (a) is actual the exact value of the ground state energy! Both (b) and (d) have values above this energy.

2 Consider a 1D system only having, i.e. $H_0 |\varphi_n\rangle = E_n |\varphi_n\rangle$, $n = 1, 2$. At $t = 0$, a perturbation $V(x,t) = V(x)$ is turned on, where V is a real function. It is also known that this perturbation has no diagonal elements when represented in $\{|\varphi_n\rangle\}$ basis, i.e. $\langle\varphi_i|V|\varphi_i\rangle = 0$. At $t = 0$, the populations of the states 1 and 2 was $P_1(0) = 1$ and $P_2(0) = 0$, respectively. Find the populations of the two states as a function of time and of the matrix elements $\langle\varphi_1|V|\varphi_2\rangle = V_{12}$ for the special case that the states are degenerate, i.e. $E_1 = E_2$. Sketch P_1 and P_2 as functions of time.

Given that $H_0 |\varphi_n\rangle = E_n |\varphi_n\rangle$ and that $V(x,t) = V(x)$ for $t > 0$, recall that the interaction picture "Schrodinger" equation becomes

$$i\hbar \frac{d}{dt} c_n(t) = \sum_m V_{nm} e^{i\omega_{nm}t} c_m(t) \tag{22}$$

where

$$\omega_{nm} = (E_n - E_m)/\hbar \tag{23}$$

Because $E_1 = E_2$ it therefore follows that $\omega_{12} = \omega_{21} = 0$. Furthermore, because there are no diagonal terms in V, we have that $V_{11} = V_{22} = 0$. Thus, the differential equation reduces to a system of two coupled ODEs.

$$i\hbar\, \dot{c}_1(t) = V_{12} c_2(t) \tag{24}$$
$$i\hbar\, \dot{c}_2(t) = V_{21} c_1(t) \tag{25}$$

using the trick from class, we can take a derivative of both equations and substitute in order to decouple.

$$i\hbar \ddot{c}_1(t) = \dot{V}_{12} c_2(t) + V_{12} \dot{c}_2(t) \tag{26}$$
$$i\hbar \ddot{c}_2(t) = \dot{V}_{21} c_1(t) + V_{21} \dot{c}_1(t) \tag{27}$$
$$\dot{c}_1 = -\frac{i}{\hbar} V_{12} c_2(t) \tag{28}$$
$$\dot{c}_2 = -\frac{i}{\hbar} V_{21} c_1(t) \tag{29}$$
$$\Rightarrow \ddot{c}_1 - \left(\frac{\dot{V}_{12}}{V_{12}}\right) \dot{c}_1 + \frac{V_{12}V_{21}}{\hbar^2} c_1 = 0 \tag{30}$$
$$\Rightarrow \ddot{c}_2 - \left(\frac{\dot{V}_{21}}{V_{21}}\right) \dot{c}_2 + \frac{V_{12}V_{21}}{\hbar^2} c_2 = 0 \tag{31}$$

We can further simplify the final two equations from above by realizing that because $V(x,t) = V(x)$, then $V_{12} = V_{12}(x)$ and $V_{21} = V_{21}(x)$ so that $\dot{V}_{12} = \dot{V}_{21} = 0$.

$$\ddot{c}_1 + \frac{V_{12}V_{21}}{\hbar^2} c_1 = 0 \tag{32}$$
$$\ddot{c}_2 + \frac{V_{12}V_{21}}{\hbar^2} c_2 = 0 \tag{33}$$

Our boundary conditions then yield $c_1(0) = 1$ and $c_2(0) = 0$ so that the time dependence of populations is given by

$$c_1(t) = \cos\left(\frac{V_{12}V_{21}}{\hbar^2}t\right) \tag{34}$$

$$c_2(t) = \sin\left(\frac{V_{12}V_{21}}{\hbar^2}t\right) \tag{35}$$

$$P_1(t) = \cos^2\left(\frac{V_{12}V_{21}}{\hbar^2}t\right) \tag{36}$$

$$P_2(t) = \sin^2\left(\frac{V_{12}V_{21}}{\hbar^2}t\right) \tag{37}$$

A sketch of the populations is shown below

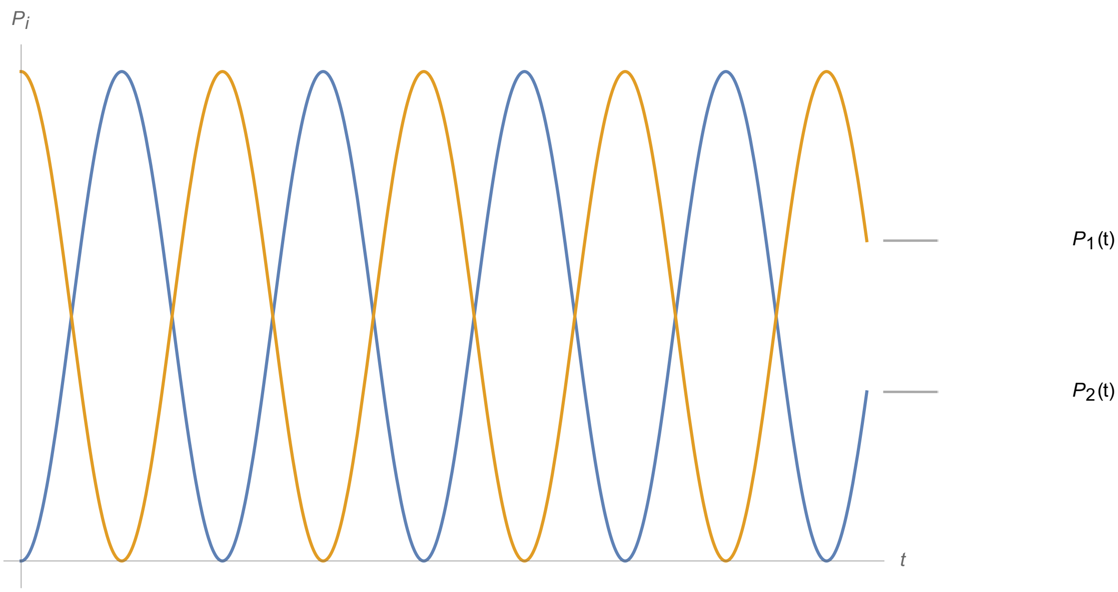

Figure 1: **Time dependent populations** figure comparing population 1 and 2.