CHEMISTRY 542

ANSWERS to FINAL Exam

December 7, 2004

In applying the principles of Quantum Mechanics in answering each question, be sure to *state the principle you are using at each step*.

1. A system has the energy eigenfunction $\Psi = C\,x \exp(ib - ax^2)$ where C, b, a are scalar constants. The zero of potential energy is taken to be the origin, i.e., $V(x=0) = 0$.
(a) Using the Schrödinger equation, ***determine the total energy of the system and the exact form of the potential energy***.
Hint: Write V(x) as $V(x) = V_0 + V_1x + V_2x^2 + V_3x^3 + \ldots$

$\mathcal{H} = p_x^2/2M + V(x)$ kinetic energy + potential energy

$\mathcal{H} = -(\hbar^2/2M)(d^2/dx^2) + V_0 + V_1x + V_2x^2 + V_3x^3 + \ldots$ Postulate 1 To every observable there corresponds an operator. The operator for p_x is $(\hbar/i)\,\partial/\partial x$

$\mathcal{H}\Psi = E\Psi$ Schrödinger equation (Postulate 2, defines eigenvalues and eigenfunction)

$$\{-(\hbar^2/2M)(d^2/dx^2) + V_0 + V_1x + V_2x^2 + V_3x^3 + \ldots\}\, C\,x \exp(ib-ax^2) = E\, C\,x \exp(ib-ax^2)$$

Given, $V(x=0) = 0 = V_0$

$$\{-(\hbar^2/2M)(d^2/dx^2) + V_1x + V_2x^2 + V_3x^3 + \ldots\}\, x \exp(ib-ax^2) = E\, x \exp(ib-ax^2)$$

Do some math:

$$d/dx\ x\exp(ib-ax^2) = \exp(ib-ax^2) + x\exp(ib-ax^2)(-2ax) = \exp(ib-ax^2) - 2ax^2\exp(ib-ax^2)$$

$$(d^2/dx^2)\, x \exp(ib-ax^2) = d/dx\,\{\exp(ib-ax^2) - 2ax^2\exp(ib-ax^2)\}$$

$$= \exp(ib-ax^2)(-2ax) - 2ax^2\exp(ib-ax^2)(-2ax) + \exp(ib-ax^2)(-4ax)$$

$$= \exp(ib-ax^2)\{-2ax + 4a^2x^3 - 4ax\} = x\exp(ib-ax^2)\{-6a + 4a^2x^2\}$$

$$\{-(\hbar^2/2M)(d^2/dx^2) + V_1x + V_2x^2 + V_3x^3 + \ldots\}\, x \exp(ib-ax^2) = E\, x \exp(ib-ax^2)$$

$$-(\hbar^2/2M)\,[-6a + 4a^2x^2]\, x\exp(ib-ax^2) + \{V_1x + V_2x^2 + V_3x^3 + \ldots\}\, x\exp(ib-ax^2) = E\, x\exp(ib-ax^2)$$

Divide the equation by $x\exp(ib-ax^2)$: (We can do this since only multiplicative operators are left in the equation.)

$$-(\hbar^2/2M)\,[-6a + 4a^2x^2] + V_1x + V_2x^2 + V_3x^3 + \ldots = E$$

Now we need to solve this equation to find the V_1, V_2, V_3, and E.
Collect coefficients of equal powers of x,

x^0: $-(\hbar^2/2M)(-6a) = E$ provides $E = 6a\,(\hbar^2/2M)$
x^1: $V_1x = 0$ provides $V_1 = 0$
x^2: $-(\hbar^2/2M)(+4a\,x^2) + V_2x^2 = 0$ provides $V_2 = 4a\,(\hbar^2/2M)$
x^3: $V_3x^3 = 0$ provides $V_3 = 0$
x^4: $V_4x^4 = 0$ provides $V_4 = 0$, also true for all higher powers of x.

Therefore, the Schrödinger equation is

$$\{-(\hbar^2/2M)\,(d^2/dx^2) + 4a\,(\hbar^2/2M)\,x^2\}\Psi = E\Psi$$

and for the eigenfunction $\Psi = C\,x\exp(ib-ax^2)$, the eigenvalue is $E = 6a\,(\hbar^2/2M)$

(b) ***Find the value of C.***

Normalization: $\int_{-\infty}^{\infty} \Psi^*\Psi dx = 1$

$\int_{-\infty}^{\infty} C^* x \exp(-ib-ax^2)\, C x \exp(ib-ax^2)\, dx = C^2 \int_{-\infty}^{\infty} x^2 \exp(-2ax^2)\, dx = 1$

$2C^2 \int_{0}^{\infty} x^2 \exp(-2ax^2)\, dx = 2C^2 [(1/8a)(\pi/2a)^{1/2}] = 1$

$C = \pi^{1/4} 2^{5/4} a^{3/4}$

2. Apply the variational method to a particle of mass M in a box of one dimension with

$V = 0$ for $-1 \le x \le 1$ and $V = \infty$ elsewhere.

Use a trial function of the form $\Psi_{\text{trial}} = 1 + c_1x^2 + c_2x^4$.

Be sure that the trial function has the proper behavior at the edge of the box.

Show <u>in detail</u> how you would find the coefficients and the approximate energy E_{var}.

Boundary conditions:

(a) For the function to be quadratically integrable,

$N^2\int_{-1}^{+1}(1 + c_1x^2 + c_2x^4)^2dx = 1$, we will find N later.

(b) Since $\Psi(x > +1) = 0$ and $\Psi(x < -1) = 0$, then, for the function to be continuous,

$\Psi_{\text{trial}}\,(x = \pm1) = 0$

$1 + c_1 + c_2 = 0$ or $c_2 = -(1 + c_1)$

$\Psi_{\text{trial}} = 1 + c_1x^2 + c_2x^4 = 1 + c_1x^2 + -(1 + c_1)x^4$

For a particle in a box of one dimension,

$\mathcal{H} = p_x^2/2M + V(x)$ kinetic energy + potential energy

$\mathcal{H} = -(\hbar^2/2M)(d^2/dx^2) + 0$ for $-1 \le x \le 1$

$$E_{\text{var}} = \frac{\int_{-1}^{1} \Psi_{trial}{}^* H \Psi_{trial}\, dx}{\int_{-1}^{1} \Psi_{trial}{}^* \Psi_{trial}\, dx}$$

$\mathcal{H}\Psi_{\text{trial}} = -(\hbar^2/2M)(d^2/dx^2)[1 + c_1x^2 + c_2x^4] = -(\hbar^2/2M)[2c_1 + 12c_2x^2]$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{\int_{-1}^{1}(1+c_1x^2+c_2x^4)(2c_1+12c_2x^2)dx}{\int_{-1}^{1}(1+c_1x^2+c_2x^4)^2 dx}$$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{\int_{-1}^{1}[2c_1+(12c_2+2c_1{}^2)x^2+14c_2c_1x^4+12c_2{}^2x^6]dx}{\int_{-1}^{1}[1+2c_1x^2+(c_1^2+2c_2)x^4+2c_2c_1x^6+c_2^2x^8]dx}$$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{\left[2c_1x+(12c_2+2c_1{}^2)x^3/3+14c_2c_1x^5/5+12c_2{}^2x^7/7\right]_{-1}^{+1}}{\left[x+2c_1x^3/3+(c_1^2+2c_2)x^5/5+2c_2c_1x^7/7+c_2^2x^9/9\right]_{-1}^{+1}}$$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{2c_1 + (12c_2 + 2c_1{}^2)/3 + 14c_2c_1/5 + 12c_2{}^2/7}{1 + 2c_1/3 + (c_1^2 + 2c_2)/5 + 2c_2c_1/7 + c_2^2/9}$$

Apply the relation $c_2 = -(1 + c_1)$ and combine terms

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{-6/7 - 48c_1/35 - 44c_1{}^2/105}{32/45 + 64c_1/315 + 8c_1^2/315}$$

Impose the condition that we want an upper bound to the energy eigenvalue,
that is, minimize E_{var} : $\partial E_{var}/\partial c_1 = 0$

$$0 = -(\hbar^2/2M) \bullet$$

$$\frac{(32/45 + 64c_1/315 + 8c_1^2/315)[-48/35 - (88/105)c_1] - (-6/7 - 48c_1/35 - 44c_1{}^2/105)[64/315 + (16/315)c_1]}{(32/45 + 64c_1/315 + 8c_1^2/315)^2}$$

$0 = 52c_1{}^2 + 571c_1 + 828$
Solve for c_1: We obtain two roots, $c_1 = = -[571 \pm (392.195]/104$
$c_1 = -9.26149$ gives $E_{\text{var}} = +23.9123\ (\hbar^2/2M)$
or $c_1 = -1.719279$ gives $E_{\text{var}} = -0.599847(\hbar^2/2M)$

E_{var} answer should be an upper bound to a positive (purely kinetic) energy !
Thus, the root $c_1 = -1.719279$ is unphysical and therefore unacceptable.
Therefore, we choose $E_{\text{var}} = +23.9123\bullet(\hbar^2/2M)$, that is, $c_1 = -9.26149$,
$c_2 = -(1+c_1) = 8.26149$

$\Psi_{\text{trial}} = N(1 + c_1x^2 + c_2x^4)$
Normalization: $1 = N^2 \int_{-1}^{+1} [1 + 2c_1x^2 + 2c_1c_2\, x^6 + (c_1{}^2 + 2c_2)x^4 + c_2{}^2x^8]\, dx$
$1 = N^2 [x + 2c_1x^3/3 + 2c_1c_2\, x^7/7 + (c_1{}^2 + 2c_2)x^5/5 + c_2{}^2x^9/9]_{-1}^{+1}$
$1 = N^2\{2 + 4\, c_1/3 + 4c_1c_2/7 + 2(c_1{}^2 + 2c_2)/5 + 2c_2{}^2/9\}$
Apply $c_2 = -(1+c_1)$,
$1 = N^2\{2 + 4\, c_1/3 - 4c_1/7 - 4c_1{}^2/7 + 2c_1{}^2/5 - 4c_1/5 - 4/5 + 2(1+2c_1+c_1{}^2)/9\}$
$1 = N^2\{28 + 8c_1 + c_1{}^2\}16/315$
$c_1 = -9.26149$ gives $2.0156585N^2 = 1$; $N = 0.704355$
Using $c_1 = -9.26149$, $c_2 = -(1+c_1) = +8.26149$, $N = 0.704355$ we find
$\Psi_{\text{trial}} = N(1 + c_1x^2 + c_2x^4) = 0.704355 - 6.523\,377\, x^2 + 5.819\,022\, x^4$
This trial function has no nodes other than at the end points $x=\pm 1$.
For the true eigenfunction of n=1 in a well of length 2 ($-1 \leq x \leq 1$), the eigenvalue is
$E = 1^2\pi^2/2^2\bullet(\hbar^2/2M) = +2.46741\bullet(\hbar^2/2M)$.
We found an upper bound to this energy, $E_{\text{var}} = +23.9123\bullet(\hbar^2/2M)$.

3. Which of the following functions, when multiplied by a normalization constant, would be acceptable one-dimensional wave functions for a bound particle and if not, why not?

(a)	$\exp[-x]$	not, function blows up at $x = -\infty$
(b)	$\exp[-x^2]$	acceptable: finite, single-valued, continuous
(c)	$x\exp[-x^2]$	acceptable: finite, single-valued, continuous
(d)	$i\exp[-x^2]$	acceptable: finite, single-valued, continuous
(e)	$f(x) = \exp[-x^2]$ for $x<0$; $f(x) = 2\exp[-x^2]$ for $x\geq 0$;	not, discontinuous at $x=0$

If A and B are two Hermitian commuting operators, and Ψ_j and Ψ_k are eigenfunctions of A with eigenvalues a_j and a_k respectively ($a_j \neq a_k$), ***prove that there are no matrix elements of B*** between states Ψ_j and Ψ_k.

Given: $A\Psi_j = a_j\Psi_j$ and $A\Psi_k = a_k\Psi_k$ (Postulate 2) and ($a_j \neq a_k$), and $AB-BA = 0$
To prove: $\int \Psi_j{}^*B\Psi_k = 0$
Proof: $\int \Psi_j{}^*(AB-BA)\Psi_k\, d\tau = 0$ since $(AB-BA) = 0$
LHS$= \int \Psi_j{}^*(AB-BA)\Psi_k\, d\tau = \int \Psi_j{}^*AB\Psi_k\, d\tau - \int \Psi_j{}^*BA\Psi_k\, d\tau$
$= \int A^*\Psi_j{}^*B\Psi_k\, d\tau - \int \Psi_j{}^*BA\Psi_k\, d\tau$ since A is a Hermitian operator.
LHS $= \int a_j\Psi_j{}^*B\Psi_k\, d\tau - \int \Psi_j{}^*B\, a_k\Psi_k\, d\tau$, Postulate 2, and the eigenvalues of a Hermitian operator are real ($a_j{}^* = a_j$).
LHS $= (a_j - a_k) \int \Psi_j{}^*B\Psi_k\, d\tau$, since B is a linear operator $B\, a_k\Psi_k = a_k\, B\Psi_k$
RHS $= 0$
Since ($a_j \neq a_k$), then the only way the LHS can be equal to zero is if $\int \Psi_j{}^*B\Psi_k\, d\tau = 0$

The energy eigenfunction of a particle in a 3-dimensional box is an eigenfunction of which of these operators?

(a)	p_x	no
(b)	$p_x{}^2$	yes
(c)	$p_z{}^2$	yes
(d)	x	no
(e)	$\partial/\partial x$	no

For the ground state of the hydrogen-like atom, ***find the average value of r, find the most probable value of r.***

the average value of r	the most probable value of r
$\Psi_{1s} = \pi^{-½}(Z/a_0)^{3/2}e^{-Zr/a0}$ $\langle r\rangle = \int\Psi_{1s}{}^*r\,\Psi_{1s}\, d\tau$ $=\pi^{-1}(Z/a_0)^3\int_0^\infty re^{-2Zr/a0}r^2dr\bullet\int_0^\pi\sin\theta d\theta\bullet\int_0^{2\pi}d\phi$ $= \pi^{-1}(Z/a_0)^3\bullet 3!/(2Z/a_0)^4\bullet 2\bullet 2\pi = (3/2)a_0$	$P(r)dr = \int_0^\pi\sin\theta d\theta\bullet\int_0^{2\pi}d\phi\bullet\Psi_{1s}{}^*\,\Psi_{1s}\, r^2dr$ $= 2\bullet 2\pi\bullet\, \pi^{-1}(Z/a_0)^3e^{-2Zr/a0}r^2dr$ $= 4(Z/a_0)^3\, e^{-2Zr/a0}\, r^2dr$ Calculus: to find the maximum probability, $dP(r)/dr = 0$ $dP(r)/dr= 4(Z/a_0)^3d/dr\, [e^{-2Zr/a0}\, r^2]$ $= 4(Z/a_0)^3e^{-2Zr/a0}\, [2r+(-2\, Z/a_0)r^2] = 0$ $r = a_0/\, Z$

True or false, ***explain your answer***

		True/ False	Explain
(a)	The state function is always equal to a function of time multiplied by a function of coordinates	F	True only if Hamiltonian for the system is not explicitly dependent on time or if it can be written as a sum of 2 parts, one part explicitly dependent on t only, the other on coordinates only
(b)	The state function is always an eigenfunction of the Hamiltonian	F	A system need not be in an eigenstate of energy
(c)	Any linear combination of eigenfunctions of the Hamiltonian is an eigenfunction of the Hamiltonian	F	True only for any linear combination of eigenfunctions with <u>same eigenvalue</u>
(d)	If the state function is not an eigenfunction of the operator A, then a measurement of the property A might give a value that is not one of the eigenvalues of A	F	See Postulate 2! The only value that a measurement of an observable can yield is one of the eigenvalues of the operator for that observable..
(e)	The probability density is independent of time for a stationary state	T	The properties of a stationary state are independent of time.
(f)	If two operators do not commute, then they cannot possess any common eigenfunctions	F	One function might be the same but not the whole set of eigenfunctions
(g)	If two operators commute, then every eigenfunction of one must be an eigenfunction of the other	F	True only for non-degenerate functions
(h)	The matrix representing a Hermitian operator is always symmetric about the diagonal	F	only true when matrix elements are real. What is true is $A_{jk} = A^*_{kj}$ (from definition of Hermitian operator)
(i)	The experimental ground state energy of the Li atom can be obtained from $E_{2s}+2E_{1s}$, where E_{2s} is the experimental energy needed to remove the 2s electron from Li and E_{1s} is the experimental energy needed to remove the 1s electron from Li	F	Let ground state energy be $-E_0$, i.e., $E_0 = E(Li^{3+}) - E(Li,1s^2 2s)$. Given $E_{2s} \equiv E(Li^+,1s^2) - E(Li,1s^2 2s)$ $E_{1s}' \equiv E(Li^{2+},1s) - E(Li^+,1s^2)$ $E_{1s}'' \equiv E(Li^{3+}) - E(Li^{2+},1s)$ we see that $E_0 = E_{2s} + E_{1s}' + E_{1s}''$ But $E_{1s} = E(Li+,1s2s) - E(Li,1s^2 2s)$ Because the 1s electrons are being removed from positively charged ions rather than the neutral atom, $E_{1s}' > E_{1s}$ and $E_{1s}'' > E_{1s}$. Thus, $E_0 >> E_{2s}+2E_{1s}$

4. For a hydrogen-like atom with Z protons in the nucleus, perturbed by a uniform applied electric field in the z direction, the perturbation Hamiltonian is

$h = e\mathcal{E}z = e\mathcal{E}r\cos\theta$, where $\mathcal{E}$ is the magnitude of the electric field.
Consider the effect of h on the n = 2 energy level, which is four-fold degenerate. Since h commutes with the angular momentum L_z, use the complex hydrogen atom orbitals 2s, $2p_0$, $2p_{+1}$ and $2p_{-1}$ which are eigenfunctions of L_z. ***Find the first order corrections to the energy and the correct zeroth order wavefunctions.***

Degenerate perturbation theory applies. Since h does not operate on ϕ, all integrals between different m_ℓ values are zero. Eigenfunctions of an operator (L_z here) which correspond to different eigenvalues, different m_ℓ, are orthogonal. Thus, we set up the matrix for h in blocks of equal m_ℓ:

$$h = \begin{array}{cccc|l} 2s & 2p_0 & 2p_{+1} & 2p_{-1} & \\ \hline 0 & A & 0 & 0 & 2s \\ A & 0 & 0 & 0 & 2p_0 \\ 0 & 0 & 0 & 0 & 2p_{+1} \\ 0 & 0 & 0 & 0 & 2p_{-1} \end{array}$$

All the diagonal elements of h matrix are zero since $\iiint \Psi_{n\ell m}{}^* r\cos\theta\,\Psi_{n\ell m}\,d\tau = \langle z\rangle = 0$ (equal contributions from + and – z values).

The h matrix is seen to be ***block diagonal*** with three small blocks to be solved:

$$2s,2p_0: \begin{vmatrix} 0 - E^{(1)} & A \\ A & 0 - E^{(1)} \end{vmatrix} = 0 \qquad 2p_{+1}: \left| 0 - E^{(1)} \right| = 0 \qquad 2p_{-1}: \left| 0 - E^{(1)} \right| = 0$$

$E^{(1)} = \pm A$ $E^{(1)} = 0$ $E^{(1)} = 0$

In other words, 2s and $2p_0$ mix and have corrections to their energy.

In the 2x2 block, Substitute $E^{(1)}$ into the first equation above, $-E^{(1)}c_1 + Ac_2 = 0$,
for $E^{(1)} = -A$ $+Ac_1 + Ac_2 = 0$ $c_1 = -c_2$ $c_1 = 2^{-½}$, $c_2 = -2^{-½}$ since $c_1{}^2 + c_2{}^2 = 1$
for $E^{(1)} = +A$ $-Ac_1 + Ac_2 = 0$ $c_1 = c_2$ $c_1 = 2^{-½}$, $c_2 = 2^{-½}$
Zeroth order eigenfunctions: $(\Psi_{2s} - \Psi_{2p0})/\sqrt{2}$; $E = -(Z^2/2^2)(e^2/2a_0) - A$
 $(\Psi_{2s} + \Psi_{2p0})/\sqrt{2}$; $E = -(Z^2/2^2)(e^2/2a_0) + A$
$2p_{+1}$ and $2p_{-1}$ remain unchanged. $\Psi_{2p\pm1}$ $E = -(Z^2/2^2)(e^2/2a_0)$
Now we just need to calculate A.
The integrals that went into the matrix are evaluated as follows, using the functions given on the last page of the exam: $\iiint \Psi_{2s}{}^* r\cos\theta\,\Psi_{2p0}\,d\tau =$

$$\frac{1}{16}\frac{Z^3}{2\pi a_0^3}\iiint\left(2-\frac{Zr}{a_0}\right)r\cos\theta\frac{Zr}{a_0}\cos\theta\exp^{-Zr/a_0}r^2dr\sin\theta d\theta d\phi$$

The first term is just like $\iiint \Psi_{2p0}{}^*\,\Psi_{2p0}\,d\tau$ except for the factor of $2a_0/Z$:

$$= \frac{2a_0}{Z} - \frac{1}{16}\frac{Z^5}{2\pi a_0^5}\int_0^\infty r^5 e^{-Zr/a_0}dr\int_0^\pi \cos^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi \; = \; \frac{2a_0}{Z} - \frac{1}{16}\frac{Z^5}{2\pi a_0^5}\bullet\frac{5!}{(Z/a_0)^6}\bullet\frac{2}{3}\bullet 2\pi$$

$$= \frac{2a_0}{Z} - \frac{5a_0}{Z} = \frac{-3a_0}{Z} \qquad \therefore A = -e\mathcal{E}\,3a_0/Z$$

In general, what would be the effect of h on any energy level (any n) of the H-like atom? Illustrate using n = 3.

For any n the wavefunctions of a H-like atom are degenerate, so we will have to set up the h matrix the same way, in blocks according to m_ℓ values, and those wavefunctions with $m_\ell = 0$ would mix. That is, ns, np_0, nd_0, … would mix together, np_{+1}, nd_{+1}, … would mix together, np_{-1}, nd_{-1}, … would mix together, and so on. Furthermore, all diagonal elements will be zero, and since $\cos\theta$ converts $\Psi_{n\ell m}$ to $\Psi_{n\ell\pm 1m}$, only adjacent ($\Delta\ell = \pm 1$) off-diagonal elements within the individual blocks are non-zero. So the h matrix for n=3 would look like

$$h = \begin{array}{ccccccccc|l}
3s & 3p_0 & 3d_0 & 3p_{+1} & 3d_{+1} & 3p_{-1} & 3d_{-1} & 3d_{+2} & 3d_{-2} & \\
\hline
0 & B & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3s \\
B & 0 & C & 0 & 0 & 0 & 0 & 0 & 0 & 3p_0 \\
0 & C & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3d_0 \\
0 & 0 & 0 & 0 & D & 0 & 0 & 0 & 0 & 3p_{+1} \\
0 & 0 & 0 & D & 0 & 0 & 0 & 0 & 0 & 3d_{+1} \\
0 & 0 & 0 & 0 & 0 & 0 & D & 0 & 0 & 3p_{-1} \\
0 & 0 & 0 & 0 & 0 & D & 0 & 0 & 0 & 3d_{-1} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3d_{+2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3d_{-2}
\end{array}$$

where the values of the only non-zero integrals are indicated by B, C, D.

5. The diamagnetic shielding of the Be nucleus by the surrounding electrons can be written in the form $B_{local} = (1-\sigma)B_0$ where B_0 is the applied magnetic field, B_{local} is the field at the nucleus and σ the nuclear magnetic shielding (which gives rise to observed NMR chemical shifts). For s electrons, σ has the form

$$\sigma = \frac{e^2}{3mc^2}\langle\sum_i \frac{1}{r_i}\rangle = 17.75\times10^{-6}\ \langle\sum_i \frac{1}{r_i}\rangle$$ with r, the distance of the electron from the nucleus, in atomic units

Show how σ for Be atom can be calculated using Slater functions. Answer must be complete but final numerical answer is not required.

In atomic units: $\langle 1/r_i\rangle$ is of the form $\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi(i)^* 1/r_i\, \Psi(i) r_i^2 dr_i \sin\theta d\theta d\phi$

$\Psi_{1s}(i) = \pi^{-1/2} Z'^{3/2} e^{-Z'r}$ using Z'= (4 - 0.30)

$\Psi_{2s}(i) = \frac{1}{4}(6\pi)^{-1/2} Z''^{5/2}\, r\, e^{-Z''r/2}$ using Z''= (4 - 2×0.85-0.35)

$\sum_i \langle 1/r_i\rangle = 2\{\pi^{-1} Z'^3 \int_0^\infty e^{-2Z'r}\, r\, dr\, 4\pi\} + 2\{(^1/_{16})(6\pi)^{-1} Z''^5 \int_0^\infty e^{-Z''r}\, r^3\, dr\, 4\pi\}$

The integrals are $\int_0^\infty e^{-2Z'r}\, r\, dr = 1/(2Z')^2$; $\int_0^\infty e^{-Z''r}\, r^3\, dr = 3!/(Z'')^4$

$\sum_i \langle 1/r_i\rangle = 2\{Z' + \frac{1}{4} Z''\} = 2\{3.7 + \frac{1}{4}(1.95)\} = 8.4$

$\sigma = 17.75\times10^{-6}\times 8.4 = 149$ ppm

Note that we have replaced $\langle\sum_i (1/r_i)\rangle$ by $\sum_i \langle 1/r_i\rangle$. This is possible because the central field Slater approximation permits us to write the Schrödinger equation in a <u>separable</u> form so that the 4-electron wavefunction becomes a simple product of 4 one-electron functions, thus we need only integrals over one-electron functions.

6. The muonic helium atom is the neutral atom system composed of a helium nucleus, an electron and a negative mu meson (or muon). A negative mu meson has the same charge as an electron (q=-e), has spin ½ and a mass 138 times that of the electron.

(i) From one point of view, the muonic helium atom is analogous to helium atom in which one electron is replaced by a negative muon. The intrinsic magnetic moment of the muon is given by $(q/2M_\mu c)g_\mu \mathbf{I}_\mu=(-e/2\cdot 138m_e c)g_\mu \mathbf{I}_\mu$ where g_μ is the muon gyromagnetic ratio which is very similar to that for an electron (2.0023), and $\mathbf{I}_\mu$ is the muon spin operator. In $He\mu^- e^-$, the electron angular momentum operator is $\mathbf{J}$ and the electron g value in this atom is g_J.

(ii) From another viewpoint, the muonic helium atom is similar to a hydrogen atom in which the proton is replaced by the pseudonucleus $(He\mu^-)^+$, since the radius of the muonic orbit in the 1s state of the muonic helium atom is small compared to that of the electron. When the He nucleus is of spin zero (^{4}He) the electron sees a *pseudonucleus with a unit positive charge and a magnetic moment equal to that of a negative muon.* Apart from the reduced mass correction, the principal difference between the electron in the muonic helium atom and the electron in the hydrogen atom is the penetration of the electron charge inside this pseudonucleus.

(a) Now consider the muonic helium atom as analogous to a hydrogen atom: $(He\mu^-)^+ e^-$, that is, as if there are only the two particles, the pseudonucleus that has angular momentum $\mathbf{I}_\mu$ and the electron that has angular momentum $\mathbf{J}$.

Find the angular momentum functions, which are the eigenfunctions of $\mathbf{F}_z = (\mathbf{I}_\mu + \mathbf{J})_z$, ***for this system in its ground state.***

In the ground state, the electron has $\ell = 0$, thus the electron has purely spin angular momentum. $\mathbf{J}_z = \mathbf{S}_z$. Let the eigenfunctions of the z component of the electron spin angular momentum be α and β for $\mathbf{J}_z$ eigenvalue $\pm \frac{1}{2}\hbar$. Let the eigenfunctions of the z component of the muon spin angular momentum be A and B for $\mathbf{I}_{\mu z}$ eigenvalue $\pm \frac{1}{2}\hbar$.

The eigenfunctions of $\mathbf{F}_z = (\mathbf{I}_\mu + \mathbf{J})_z$ are the products of the functions and the corresponding eigenvalues are the sums, (separation of variables):

Aα	$+1\hbar$	that is $\mathbf{F}_z A\alpha = +1\hbar\, A\alpha$
Bβ	$-1\hbar$	$\mathbf{F}_z A\alpha = -1\hbar\, B\beta$
Aβ	$0\hbar$	$\mathbf{F}_z A\alpha = 0\hbar\, A\beta$
Bα	$0\hbar$	$\mathbf{F}_z A\alpha = 0\hbar\, B\alpha$

(b) ***Find the linear combinations of these functions that are eigenfunctions of*** $\mathbf{F}^2$.

Since $\mathbf{F}$ is angular momentum, then the eigenvalues of $\mathbf{F}_z$ $+1\hbar$, $-\hbar$, $0\hbar$ go with the eigenvalue of $\mathbf{F}^2$ that is $1(1+1)\hbar^2$ and the eigenvalues of $\mathbf{F}_z$ $0\hbar$ goes with the eigenvalue of $\mathbf{F}^2$ that is $0(0+1)\hbar^2$. Since there are two functions which have $\mathbf{F}_z$ eigenvalues $0\hbar$, we have to form linear combinations, one of which give $\mathbf{F}^2$ eigenvalue $= 1(1+1)\hbar^2$ and the other gives $\mathbf{F}^2$ eigenvalue $= 0(0+1)\hbar^2$

Aα	$\mathbf{F}_z A\alpha = +1\hbar\, A\alpha$	$\mathbf{F}^2 A\alpha = 1(1+1)\hbar^2\, A\alpha$
Bβ	$\mathbf{F}_z A\alpha = -1\hbar\, B\beta$	$\mathbf{F}^2 B\beta = 1(1+1)\hbar^2\, B\beta$
$(A\beta + B\alpha)/\sqrt{2}$	$\mathbf{F}_z (A\beta + B\alpha)/\sqrt{2} = 0\hbar(A\beta + B\alpha)/\sqrt{2}$;	$\mathbf{F}^2 (A\beta + B\alpha)/\sqrt{2} = 0\hbar(A\beta + B\alpha)/\sqrt{2}$
$(A\beta - B\alpha)/\sqrt{2}$	$\mathbf{F}_z (A\beta - B\alpha)/\sqrt{2} = 0\hbar(A\beta - B\alpha)/\sqrt{2}$;	$\mathbf{F}^2 (A\beta - B\alpha)/\sqrt{2} = 0\hbar(A\beta - B\alpha)/\sqrt{2}$

(c) In a static magnetic field $\mathbf{B}_0$, the relevant part of the Hamiltonian for the ground state of $(^4\mathrm{He}\mu^-)\,e^-$ is

$$a(\mathbf{I}_\mu \bullet \mathbf{J}) + - (-e/2m_ec)g_J\mathbf{J}\bullet\mathbf{B}_0 + -(-e/2\cdot 138m_ec)g_\mu\mathbf{I}_\mu \bullet\mathbf{B}_0$$

where a is the hyperfine coupling constant that is a measure of the energy of interaction between the two magnetic moments. Draw an energy level diagram, energy along the y axis and magnitude of $\mathbf{B}_0$ along the x axis, that illustrates how the energies calculated from this Hamiltonian would vary from $\mathbf{B}_0 = 0$ to higher values of magnetic field. Label the states with F, M_F, M_J, M_μ quantum numbers as appropriate.

Hint: Use perturbation theory: Think of the two limiting cases $B_0 = 0$ and B_0 very large. The z axis is along B_0. At each limit, consider which of the 3 terms in the above Hamiltonian you should assign to $\mathcal{H}^{(0)}$ and which to h, and find the zeroth order functions and $E^{(0)}$ that you will have. Draw the levels at each limit and then simply connect which levels become which.

(1) At the $\mathbf{B}_0 = 0$ limit $\mathcal{H}^{(0)} = a(\mathbf{I}_\mu \bullet \mathbf{J})$ and $\boldsymbol{h} = (e/2m_ec)g_J\mathbf{J}\bullet\mathbf{B}_0 + (e/2\cdot 138m_ec)g_\mu\mathbf{I}_\mu \bullet\mathbf{B}_0$ Thus the energy levels and zeroth order functions at this end are those which we found above, Aα, Bβ, (Aβ + Bα)/√2 , (Aβ - Bα)/√2, with energies that depend on the hyperfine coupling a and the quantum numbers that give the eigenvalues of $\mathbf{F}^2$, with the different M_F = 0, 1, -1 for F = 1 being degenerate since $\mathbf{B}_0 = 0$.

(2) In the other limit, with $\mathbf{B}_0$ very large, $\mathcal{H}^{(0)} = (e/2m_ec)g_J\mathbf{J}\bullet\mathbf{B}_0 + (e/2\cdot 138m_ec)g_\mu\mathbf{I}_\mu \bullet\mathbf{B}_0$ and $\boldsymbol{h} = a(\mathbf{I}_\mu \bullet \mathbf{J})$. Obviously at this limit the energy levels and zeroth order functions are without the coupling of angular momentum that comes in $\boldsymbol{h}$. So the zeroth order functions are Aα, Bβ, Aβ, Bα, with energies that are given by

$E^{(0)} = (e/2\cdot 138m_ec)g_\mu(\pm\tfrac{1}{2}\hbar)\mathbf{B}_0 + (e/2m_ec)g_J(\pm\tfrac{1}{2}\hbar)\mathbf{B}_0$

where the functions A, B correspond to $+\tfrac{1}{2}\hbar$, $-\tfrac{1}{2}\hbar$ respectively in the first term and the functions α,β correspond to $+\tfrac{1}{2}\hbar$, $-\tfrac{1}{2}\hbar$ respectively in the second term. Splitting between the ±½ states for the electron is factor of 138 greater than the ±½ splitting for the muon.

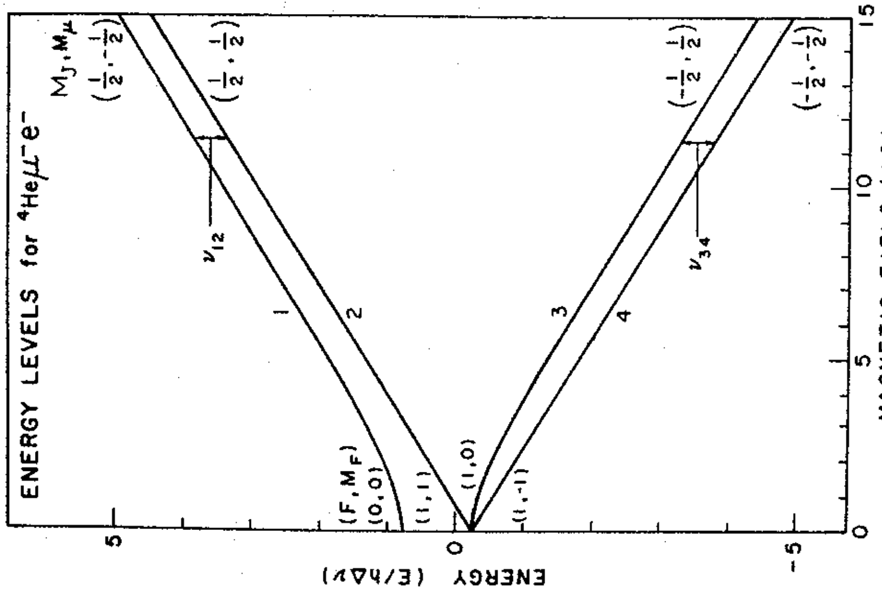


FIG. 1. Energy-level diagram for $^4\mathrm{He}\mu^-e^-$ in the ground state in a magnetic field. The states are labeled 1–4 for convenience.

(d) Now consider the muonic helium atom as analogous to a normal helium atom. *Assume that you have separated out the translational motion of the entire atom.* ***Write the non-relativistic, time independent Schrödinger equation for this atom. Do you have to worry about anti-symmetrization?***

$\{- (\hbar^2/2M_\mu)\nabla_\mu^2 - (\hbar^2/2m_e)\nabla_e^2 - 2e^2/r_\mu - 2e^2/r_e + e^2/r_{e\text{-}\mu}\}\ \Psi(\mathbf{r}_\mu, \mathbf{r}_e) = E\ \Psi(\mathbf{r}_\mu, \mathbf{r}_e)$

No because the electron and muon are distinguishable particles so can not be permuted

To solve the problem of electron-muon repulsion, think about the fact that the radius of the muonic orbit in the 1s state of the muonic helium atom is small compared to that of the electron (the mass of the muon is 138 times that of an electron). As a consequence, the screening by the muon of the nuclear charge seen by the electron is nearly complete, whereas the muon is hardly screened by the electron. From the muon's point of view what would be the nuclear charge close to? From the electron's point of view, what would be the nuclear charge close to? On this basis, write down the Schrödinger equation that approximately describes the system and find its solutions.

The muon sees a charge of $Z_{eff} = 2$, whereas the electron sees a charge of $Z_{eff} = 1$. Thus approximately, we have

$\{- (\hbar^2/2M_\mu)\nabla_\mu^2 - (\hbar^2/2m_e)\nabla_e^2 - 2e^2/r_\mu - 1e^2/r_e\}\ \Psi(\mathbf{r}_\mu, \mathbf{r}_e) = E\ \Psi(\mathbf{r}_\mu, \mathbf{r}_e)$

This is a separable problem, Let $\Psi(\mathbf{r}_\mu, \mathbf{r}_e) = \Psi(\mathbf{r}_\mu)\bullet\Psi(\mathbf{r}_e)$

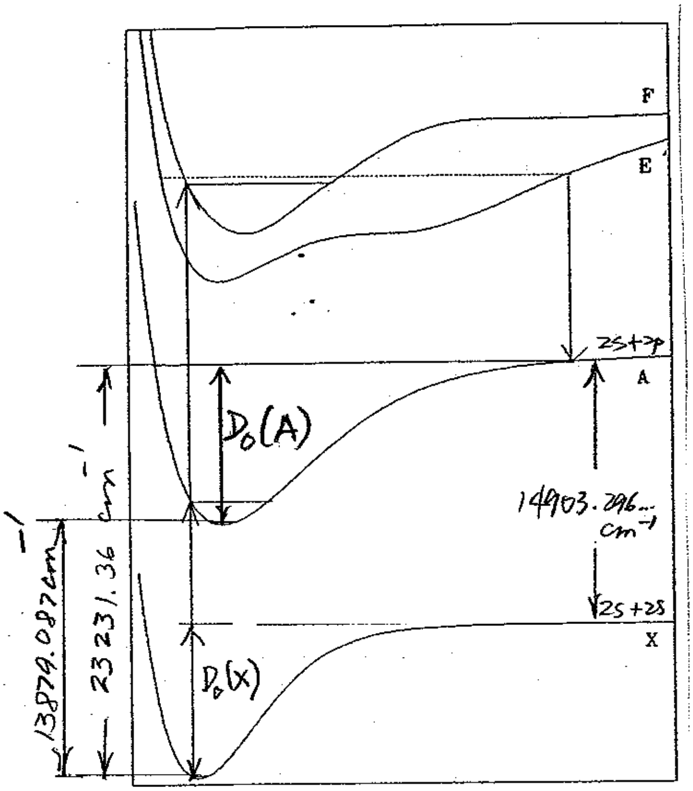
(1) $\{ - (\hbar^2/2m_e)\nabla_e^2 - 1e^2/r_e \}\ \Psi(\mathbf{r}_e) = E_e\Psi(\mathbf{r}_e)$ with solutions that are hydrogen atom functions $\Psi_{n\ell m}$ with Z=1. E_e are hydrogen atom energies $-(1^2/n^2)(e^2/2a_0)$.

(2) $\{- (\hbar^2/2M_\mu)\nabla_\mu^2 - 2e^2/r_\mu\}\Psi(\mathbf{r}_\mu) = E_\mu\Psi(\mathbf{r}_\mu)$ with solutions that are hydrogen atom functions $\Psi_{n\ell m}$ with Z=2, and energies $E_\mu = -(2^2/n^2)(e^2/2a)$ except that the reduced mass and therefore the a (not a_0!)in the functions and energy must use the correct reduced mass (not m_e) but a reduced mass taken from $1/M_{\text{He nucleus}} + 1/138m_e$.

If we use perturbation theory, we can put back the part that was left out in the above treatment. ***What do we need to use for h***?

h $= + e^2/r_{e\text{-}\mu} - 1e^2/r_e$

7. Some of the states of the Li_2 molecule are shown in the diagram below:
[from C. Linton et al., *J. Mol.. Spectrosc.* **175**, 340 (1996)]



This paper is a study of the A state of Li_2 From v=0 up to v=84 of the A state was observed, extrapolation to v=109 (the dissociation limit) was possible. X is the ground state. There are other excited states besides those shown in the figure, in particular there is a $B^1\Pi_u$, and a $G^1\Pi_g$. The A state dissociates to the atomic $(2s)^2S_{1/2}$ + $(2p)^2P_{1/2}$ states. The energy difference between the Li atom states $E[(2p)^2P_{1/2}] - E[(2s)^2S_{1/2}]$ is known accurately as 14903.296792 cm^{-1}. From the ground state v=0 to the dissociation limit of the A state is 23231.36 cm^{-1}. From the ground state v=0 to the A v=0 is 13879.087 cm^{-1}. In this work, the information from 84 vibrational levels in the A state permits a very accurate determination of the potential function which is shown in the figure.

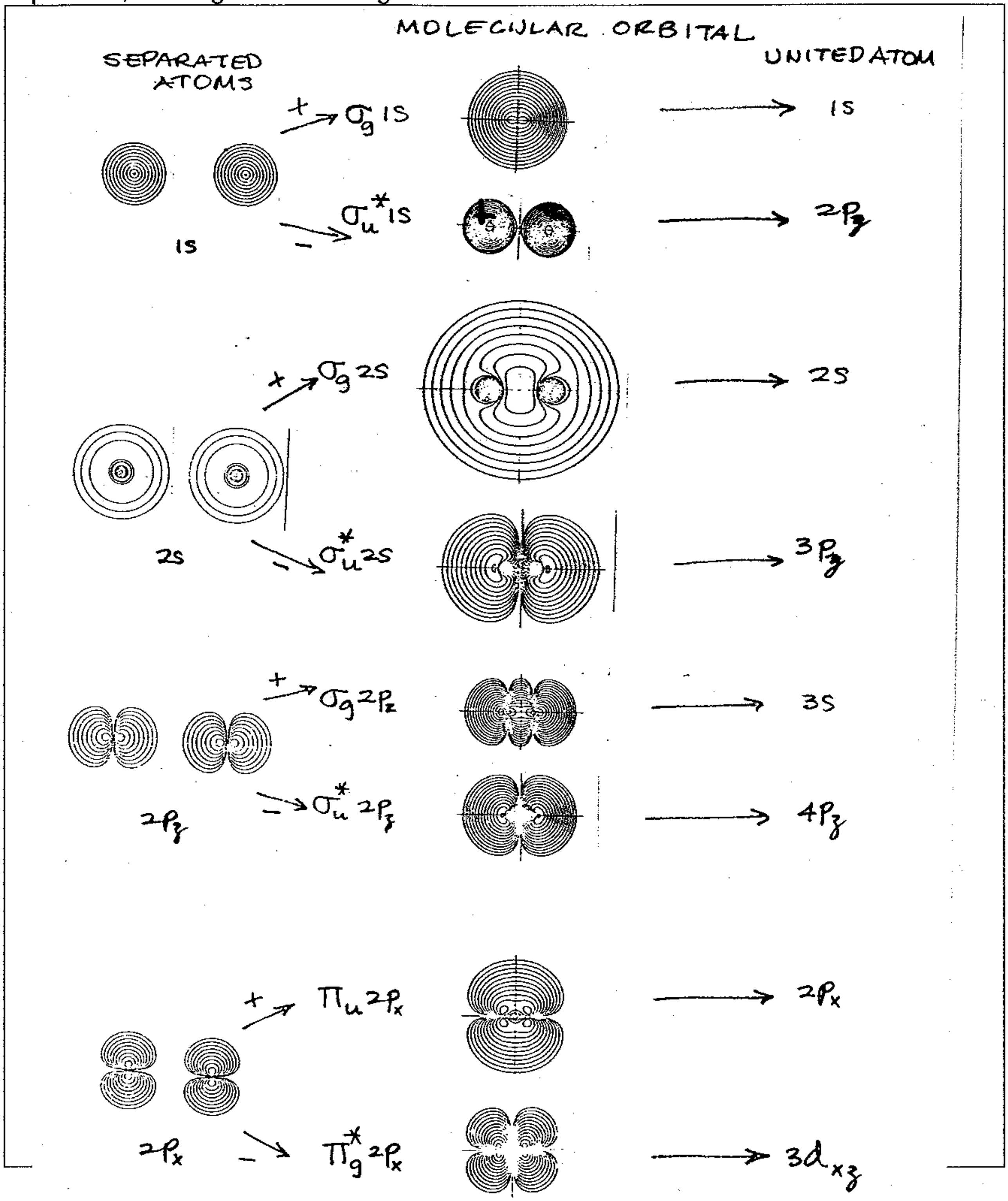
(a) From the given data, it is possible to determine the dissociation energy, D_0, of the ground state X. ***Find it***, you may give your answer in units of cm^{-1}.

23,231.36 – 14903.2968792 = 8328.06 cm^{-1} = D_0 of the ground state X

(b) From the given data, it is possible to determine the dissociation energy, D_0, of the state A. ***Find it***, you may give your answer in units of cm^{-1}.

23,231.36 – 13879.087 = 9352.273 cm^{-1} = D_0 of the state A

(c) From the electronic configuration of the atoms, use linear combinations of atomic orbitals to discover the MOs that can be formed when they overlap with + or – coefficients. Include <u>all</u> electrons. Draw the MOs (sketch contour plots or Jorgensen-Salem orbital pictures) indicating signs of the wavefunction in the various regions. Assign complete MO labels including the value of λ, symmetry with respect to i operation, bonding or antibonding.



(See orbital pictures on previous page). Below is additional information showing how electronic configurations using these molecular orbitals from part (c) lead to various states.

Li($1s^2 2s$) +L($1s^2 2s$): $1s+1s \rightarrow \sigma_g 1s$; $1s-1s \rightarrow \sigma_u{}^* 1s$; $2s+2s \rightarrow \sigma_g 2s$
Thus, the 6-electron configuration is $(\sigma_g 1s)^2(\sigma_u{}^* 1s)^2(\sigma_g 2s)^2$ which gives rise to X state

Li($1s^2 2s$) +L($1s^2 2p$): $1s+1s \rightarrow \sigma_g 1s$; $1s-1s \rightarrow \sigma_u{}^* 1s$; $2s+2p_0 \rightarrow \sigma_g(2s+2p_0)$
$2s-2p_0 \rightarrow \sigma_u{}^*(2s-2p_0)$
(see $2s+2p_{\pm 1}$ below)
Thus, the 6-electron configuration is $(\sigma_g 1s)^2(\sigma_u{}^* 1s)^2(\sigma_g)^2 \rightarrow S=0,\ {}^1\Sigma_g{}^+$
or $(\sigma_g 1s)^2(\sigma_u{}^* 1s)^2(\sigma_u{}^*)^2 \rightarrow S=0,\ {}^1\Sigma_g{}^+$
or $(\sigma_g 1s)^2(\sigma_u{}^* 1s)^2(\sigma_g)^1(\sigma_u{}^*)^1 \rightarrow S=0$ or 1, ${}^1\Sigma_u{}^+, {}^3\Sigma_u{}^+$

Li($1s^2 2s$) +L($1s^2 2p$): $1s+1s \rightarrow \sigma_g 1s$; $1s-1s \rightarrow \sigma_u{}^* 1s$; $2s+2p_{\pm 1} \rightarrow \pi_u$
$2s-2p_{\pm 1} \rightarrow \pi_u{}'^*$
Consider $(\pi_u)^2$: 6-electron configuration is $(\sigma_g 1s)^2(\sigma_u{}^* 1s)^2(\pi_u)^2$
$\Lambda=+1-1=0$ and $-1+1=0$ since identical atoms, equivalent orbitals, form linear combns:
$[\pi^+(1)\bullet\pi^-(2) + \pi^+(2)\bullet\pi^-(1)] \bullet [\alpha(1)\beta(2) - \alpha(2)\beta(1)]/2 \rightarrow S=0$, parity=+, that is, ${}^1\Sigma_g{}^+$
$[\pi^+(1)\bullet\pi^-(2) - \pi^+(2)\bullet\pi^-(1)] \bullet [\alpha(1)\,\alpha(2)]$ etc. $\rightarrow S=1$, parity=-, that is, ${}^3\Sigma_g{}^-$
$\Lambda=+1+1=+2$ and $-1-1=-2$
$[\pi^+(1)\bullet\pi^+(2)] \bullet [\alpha(1)\beta(2) - \alpha(2)\beta(1)]/\sqrt{2}$ and
$[\pi^-(1)\bullet\pi^-(2)] \bullet [\alpha(1)\beta(2) - \alpha(2)\beta(1)]/\sqrt{2} \rightarrow$ both $S=0$, parity= ±, that is, ${}^1\Delta_g$
Other configurations: using σ_g and $\sigma_u{}^*$ and π_u
Consider $(\sigma_g)^1(\pi_u)^1$ $\Lambda=0+1=+1$ and $0-1=-1$, $\rightarrow$ u, Π, S=0 or 1, that is, ${}^1\Pi_u, {}^3\Pi_u$
Consider $(\sigma_u{}^*)^1(\pi_u)^1$ $\Lambda=0+1=+1$ and $0-1=-1$, $\rightarrow$ g, Π, S=0 or 1, that is, ${}^1\Pi_g, {}^3\Pi_g$

Recall from Herzberg Chap VI that there are three ways to find the term symbols for states of a diatomic molecule: from the state of the united atom (which we skipped), from the electronic configuration shown above on this page, and from the term symbols of the atoms into which the diatomic molecule dissociates, shown in part (e) on the following page. Just for fun, compare the results from the last two methods.

(d) Draw the correlation diagram that connects these orbitals, from separated atoms to molecule to united atom. Label all orbitals completely

See correlations in orbital pictures on previous page. Below is how the united atom state is found:

We make use of the principle that Λ is conserved in going from separate atoms to diatomic molecule to united atom. Also, symmetry with respect to $\boldsymbol{i}$ (g or u) is conserved.

This means that for σ_g the correlations are: $(m_{\ell 1}=0, m_{\ell 2}=0) \rightarrow \sigma_g \rightarrow m_{\ell \text{united}}=0$
$(1s+1s) \rightarrow \sigma_g \rightarrow 1s$
$(2s+2s) \rightarrow \sigma_g \rightarrow 2s$
$(2p_0+2p_0) \rightarrow \sigma_g \rightarrow 3s$
$(3s+3s) \rightarrow \sigma_g \rightarrow 3d_0$

This means that for σ_u the correlations are: $(m_{\ell 1}=0, m_{\ell 2}=0) \rightarrow \sigma_u \rightarrow m_{\ell \text{united}}=0$
$(1s-1s) \rightarrow \sigma_u^* \rightarrow 2p_0$
$(2s-2s) \rightarrow \sigma_u^* \rightarrow 3p_0$
$(2p_0-2p_0) \rightarrow \sigma_u^* \rightarrow 4p_0$
$(3s-3s) \rightarrow \sigma_u^* \rightarrow 5p_0$

Similarly for π_u: $(m_{\ell 1}=1, m_{\ell 2}=1) \rightarrow \pi_u \rightarrow m_{\ell \text{united}}=\pm 1$
$(2p_x+2p_x) \rightarrow \pi_u \rightarrow 2p_x$

Similarly for π_g: $(m_{\ell 1}=1, m_{\ell 2}=1) \rightarrow \pi_g \rightarrow m_{\ell \text{united}}=\pm 1$
$(2p_x-2p_x) \rightarrow \pi_g^* \rightarrow 3d_{xz}$

$Li+Li \rightarrow Li_2 \rightarrow C$

We use an energy-ordered list at both ends so as to connect corresponding ones. The united atom orbitals are those of carbon.

(e) From the electronic configuration and term symbols of the Li atoms into which the given A state of Li_2 molecule is known to dissociate (given), determine all the possible Li_2 molecular states that dissociate into these atomic states. One of them is the A state. This example is the $^2S_g + ^2P_u$ for like atoms different states, that I did in lecture.

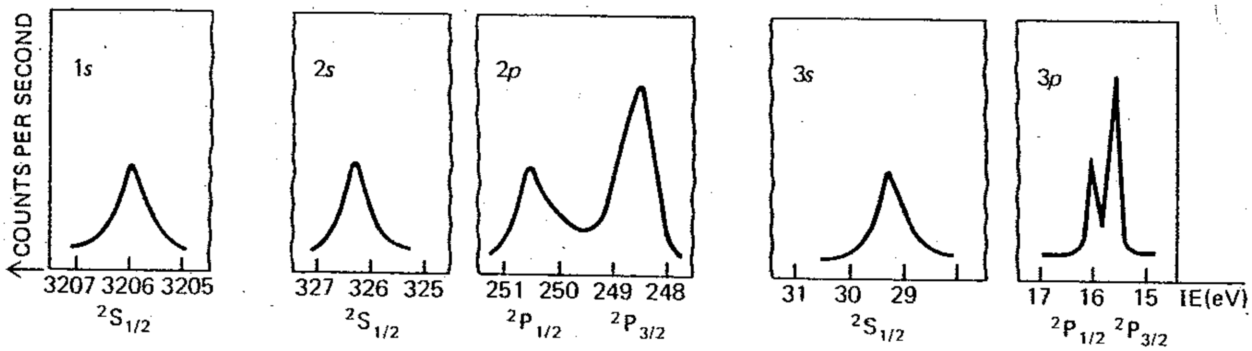
Atom 1: $1s^2 2s$: $L_1=0$, $S_1=\frac{1}{2}$, gives $2S+1=2$, $\sum_i \ell_i=0$ gives g $\therefore {}^2S_g$ is the atomic state
Atom 2: $1s^2 2p$: $L_1=1$, $S_1=\frac{1}{2}$, gives $2S+1=2$, $\sum_i \ell_i=1$ gives u $\therefore {}^2P_u$ is the atomic state

To make the molecular states find the λ values that result from all possible combinations of M_{L1} and M_{L2}:

$1={}^2S_g$	$2={}^2P_u$	λ, S	Λ symbol 2S+1	parity sign	g or u	Term symbol
$M_L=0$, $S=\frac{1}{2}$	$M_L=0$ $S=\frac{1}{2}$	0, S=0,1	Σ 2S+1=1,3		like atoms, g and u	${}^1\Sigma^+{}_g, {}^1\Sigma^+{}_u, {}^3\Sigma^+{}_g, {}^3\Sigma^+{}_u$
$M_L=0$, $S=\frac{1}{2}$	$M_L=\pm 1$ $S=\frac{1}{2}$	± 1 S=0,1	Π 2S+1=1,3		like atoms, g and u	${}^1\Pi_g, {}^1\Pi_u, {}^3\Pi_g, {}^3\Pi_u$
L=0, $\sum_i \ell_i=0$	L=1, $\sum_i \ell_i=1$			sum =0+0+1+1= even, + for all Σ		

Although like atoms, they are in different states, so all terms are allowed: half of the g or u set comes from $1={}^2S_g$, $2={}^2P_u$, and half comes from $1={}^2P_u$, $2={}^2S_g$. Of these term symbols, one is the A state, and the $B^1\Pi_u$ and $G^1\Pi_g$ have been mentioned also. Since the ground state is $X^1\Sigma^+{}_g$, then A must be singlet and u: ${}^1\Sigma^+{}_u$ for electric dipole allowed transitions.

8. (a) By photoelectron spectroscopy, XPES, or ESCA or variants thereof, a variety of ionization energies are found for the atoms of a sample. In this analytical technique, the sample is irradiated with high energy radiation and electrons are expelled. Some of the energy of the incident radiation is carried off as kinetic energy of the expelled electrons. The energy required to produce a particular ionization is equal to the energy of the incident photon ($h\nu$) less the kinetic energy of the expelled electrons (ε_{kin}). The pattern of electron kinetic energies thus yields a display (spectrum) of the various ionization energies of the atoms or molecules of a sample. Now, if we have a model of an atom, such as Slater model, in which the energy of the atom for a given electronic configuration can be written in terms of a sum over the one-electron-at-a-time (i.e., orbital) energies, then the measured ionization energies serve as measures of the orbital energies. The ionization spectrum of argon is shown below:



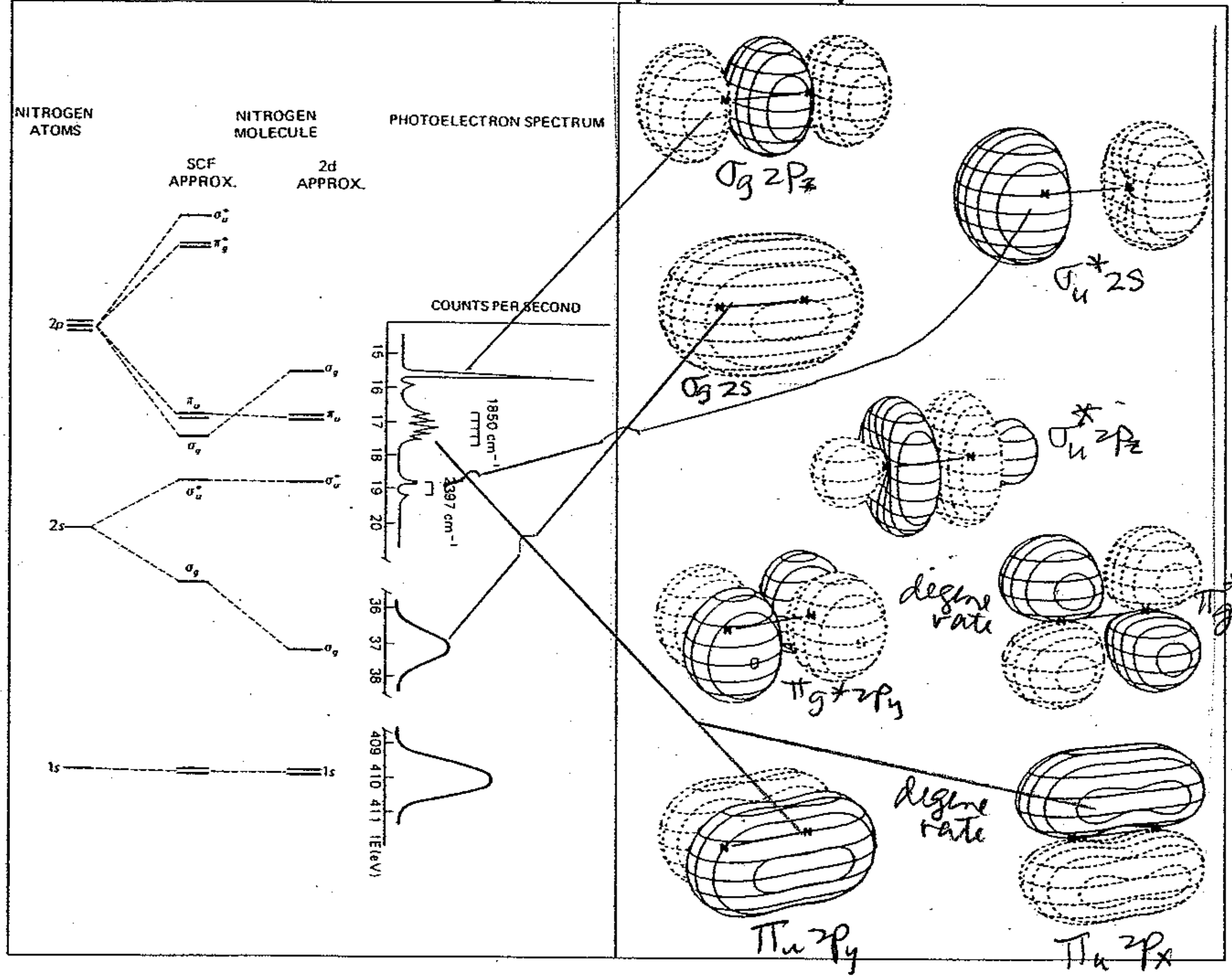
The orbital of the parent argon atom from which an electron has been expelled in each case is shown as label within the frame. For each of the 5 frames ***write under each frame the atomic term symbol*** for the Ar^+ ion formed. Write down the ***electronic configuration of the ion*** that is produced for each peak and where two peaks occur in a frame, ***provide an explanation.*** Why smaller splitting in 3p?

	Electronic configuration of Ar^+ ion	Term symbol	Why two peaks?
1s	$1s^12s^22p^63s^23p^6$	$^2S_{1/2}$	
2s	$1s^22s^12p^63s^23p^6$	$^2S_{1/2}$	
2p	$1s^22s^22p^53s^23p^6$	$^2P_{1/2}$ and $^2P_{3/2}$	**L** and **S** vectors couple with each other via the perturbation term $\zeta\mathbf{L}\bullet\mathbf{S}$ since $L\neq0$ for the ion: $L=1$ and $S=½$, giving rise to $J=½$ and $^3/_2$ ion states: $^2P_{1/2}$ and $^2P_{3/2}$
3s	$1s^22s^22p^63s^13p^6$	$^2S_{1/2}$	
3p	$1s^22s^22p^63s^23p^5$	$^2P_{1/2}$ and $^2P_{3/2}$	same reason as 2p, except ζ is smaller since Z_{eff} for 3p is smaller than for 2p and ζ depends on Z_{eff}^4

(b) For each of the 5 frames how would one estimate [E(Ar^+) – E(Ar)]? ***Do one example.***

The easiest one to do is the loss of 3s or 3p. Using Slater's approximation,
s(3p or 3s) = 0.35x7 +0.85x8 +1.00x2 = 11.25 for the neutral atom
s(3p or 3s) = 0.35x6 +0.85x8 +1.00x2 = 10.9 for the Ar^+ ion
s(2s or 2p), s(1s) are unchanged for both neutral and ion
$[E(Ar^+) - E(Ar)] = [-7(18-10.9)^2/3^2 - -8(18-11.25)^2/3^2](e^2/2a_0)=[-39.2+40.5]\ (e^2/2a_0)=17.7\text{eV}$
All the other terms, $-2(18 - 0.30)^2/1^2 - 8(18 - 0.35\text{x}7 - 0.85\text{x}2)^2/2^2$ appear in both neutral and ion and therefore subtract out in taking the difference.

(c) Below we see the molecular orbital energies of N_2 molecule can be related to its photoelectron spectrum [in which one electron is kicked off by a photon, leaving an ion; various ionization energies are found, just as in atoms. The one-electron functions (molecular orbitals) for N_2 are shown on the right, in randomized order. ***Draw a line connecting the orbitals on the right to the peaks in the spectrum on the left.***



(d) ***Assign an MO designation (to each orbital on the right)*** to provide information about its behavior upon the ***i*** operation, its angular momentum, and the atomic orbitals that carry the largest coefficients in the linear combination that constitutes the function.

LONGER ANSWER to 2:

2. Apply the variational method to a particle of mass M in a box of one dimension with $V = 0$ for $-1 \leq x \leq 1$ and $V = \infty$ elsewhere.
Use a trial function of the form $\Psi_{\text{trial}} = 1 + c_1x^2 + c_2x^4$.
Be sure that the trial function has the proper behavior at the edge of the box.
Show in detail how you would find the coefficients and the approximate energy E_{var}.

Boundary conditions:
(a) For the function to be quadratically integrable,

$N^2\int_{-1}^{+1}(1 + c_1x^2 + c_2x^4)^2dx = 1$,   we will find N later.

(b) Since $\Psi(x > +1) = 0$ and $\Psi(x < -1) = 0$, then, for the function to be continuous,

$\Psi_{\text{trial}}\ (x = \pm 1) = 0$
$1 + c_1 + c_2 = 0$ or $c_2 = -\ (1 + c_1)$
$\Psi_{\text{trial}} = 1 + c_1x^2 + c_2x^4 = 1 + c_1x^2 + -\ (1 + c_1)x^4$

For a particle in a box of one dimension,
$\mathcal{H} = p_x^2/2M + V(x)$ kinetic energy + potential energy
$\mathcal{H} = -(\hbar^2/2M)(d^2/dx^2)\ + 0$ for $-1 \leq x \leq 1$

$$E_{\text{var}} = \frac{\int_{-1}^{1}\Psi_{trial}{}^{*}H\Psi_{trial}dx}{\int_{-1}^{1}\Psi_{trial}{}^{*}\Psi_{trial}dx}$$

$\mathcal{H}\Psi_{\text{trial}} = -(\hbar^2/2M)(d^2/dx^2)[\,1 + c_1x^2 + c_2x^4\,] = -(\hbar^2/2M)\,[\,2c_1 + 12c_2x^2\,]$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{\int_{-1}^{1}(1+c_1x^2+c_2x^4)(2c_1+12c_2x^2)dx}{\int_{-1}^{1}(1+c_1x^2+c_2x^4)^2dx}$$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{\int_{-1}^{1}[2c_1+(12c_2+2c_1{}^2)x^2+(12c_2c_1+2c_2c_1)x^4+12c_2{}^2x^6]dx}{\int_{-1}^{1}[1+2c_1x^2+(c_1^2+2c_2)x^4+2c_2c_1x^6+c_2^2x^8]dx}$$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{\int_{-1}^{1}[2c_1+(12c_2+2c_1{}^2)x^2+14c_2c_1x^4+12c_2{}^2x^6]dx}{\int_{-1}^{1}[1+2c_1x^2+(c_1^2+2c_2)x^4+2c_2c_1x^6+c_2^2x^8]dx}$$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{\left[2c_1x+(12c_2+2c_1{}^2)x^3/3+14c_2c_1x^5/5+12c_2{}^2x^7/7\right]_{-1}^{+1}}{\left[x+2c_1x^3/3+(c_1^2+2c_2)x^5/5+2c_2c_1x^7/7+c_2^2x^9/9\right]_{-1}^{+1}}$$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{4c_1+(24c_2+4c_1{}^2)/3+28c_2c_1/5+24c_2{}^2/7}{2+4c_1/3+2(c_1^2+2c_2)/5+4c_2c_1/7+2c_2^2/9}$$

Divide out the factor of 2 from numerator and denominator,

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{2c_1 + (12c_2 + 2c_1^2)/3 + 14c_2c_1/5 + 12c_2^2/7}{1 + 2c_1/3 + (c_1^2 + 2c_2)/5 + 2c_2c_1/7 + c_2^2/9}$$

Apply the relation $c_2 = -(1 + c_1)$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{2c_1 - 4 - 4c_1 + 2c_1^2/3 - 14c_1/5 - 14c_1^2/5 + 12c_1^2/7 + 24c_1/7 + 12/7}{1 + 2c_1/3 + c_1^2/5 - 2c_1/5 - 2/5 - 2c_1/7 - 2c_1^2/7 + c_1^2/9 + 2c_1/9 + 1/9}$$

$$E_{\text{var}} = -(\hbar^2/2M) \bullet \frac{-6/7 - 48c_1/35 - 44c_1^2/105}{32/45 + 64c_1/315 + 8c_1^2/315}$$

Impose the condition that we want an upper bound to the energy eigenvalue,
that is, minimize E_{var} : $\partial E_{var}/\partial c_1 = 0$

$0 = -(\hbar^2/2M) \bullet$

$$\frac{(32/45 + 64c_1/315 + 8c_1^2/315)[-48/35 - (88/105)c_1] - (-6/7 - 48c_1/35 - 44c_1^2/105)[64/315 + (16/315)c_1]}{(32/45 + 64c_1/315 + 8c_1^2/315)^2}$$

$0 = (224+64c_1+8c_1^2)(-144-88c_1) + (90+144c_1+44c_1^2)(64+16c_1)$

$0 = (56+16c_1+2c_1^2)(-18-11c_1) + (45+72c_1+22c_1^2)(4+c_1)$

$0 = 52c_1^2 + 571c_1 + 828$

Solve for c_1: We obtain two roots, $c_1 = = -[571 \pm (392.195]/104$

$c_1 = -9.26149$ gives $E_{\text{var}} = +23.9123\ (\hbar^2/2M)$

or $c_1 = -1.719279$ gives $E_{\text{var}} = -0.599847(\hbar^2/2M)$

E_{var} answer should be an upper bound to a positive (purely kinetic) energy !
Thus, the root $c_1 = -1.719279$ is unphysical and therefore unacceptable.
Therefore, we choose $E_{\text{var}} = +23.9123\bullet(\hbar^2/2M)$, that is, $c_1 = -9.26149$,

$c_2 = -(1+c_1) = 8.26149$

$\Psi_{\text{trial}} = N(1 + c_1x^2 + c_2x^4)$

Normalization: $= N^2 \int_{-1}^{+1} [1 + 2c_1x^2 + 2c_1c_2 x^6 + (c_1^2 + 2c_2)x^4 + c_2^2x^8]\, dx = 1$

$= N^2 [x + 2c_1x^3/3 + 2c_1c_2 x^7/7 + (c_1^2 + 2c_2)x^5/5 + c_2^2x^9/9]_{-1}^{+1} = 1$

$= N^2 \{2 + 4c_1/3 + 4c_1c_2/7 + 2(c_1^2 + 2c_2)/5 + 2c_2^2/9\} = 1$

Apply $c_2 = -(1+c_1)$,

$= N^2 \{2 + 4c_1/3 - 4c_1/7 - 4c_1^2/7 + 2c_1^2/5 - 4c_1/5 - 4/5 + 2(1+2c_1+c_1^2)/9\} = 1$

$1 = N^2 \{2 - 4/5 + 2/9 + [4/3 - 4/7 - 4/5 + 4/9]\, c_1 + [-4/7 + 2/5 + 2/9]\, c_1^2\}$

$1 = N^2 \{64/45 + (128/315)\, c_1 + (16/315)\, c_1^2\}$

$1 = N^2 \{64/45 + (128/315)\, c_1 + (16/315)\, c_1^2\} = N^2 \{28 + 8c_1 + c_1^2\}16/315$

$c_1 = -9.26149$ gives $2.0156585N^2 = 1$; $N = 0.704355$

With the normalization constant we could write directly

$E_{\text{var}} = -(\hbar^2/2M) \bullet N^2\, 2\{-6/7 - 48c_1/35 - 44c_1^2/105\} = +23.9123\ (\hbar^2/2M)$ the same answer.

Using $c_1 = -9.26149$, $c_2 = -(1+c_1) = +8.26149$, $N = 0.704355$ we find

$\Psi_{\text{trial}} = N(1 + c_1x^2 + c_2x^4) = 0.704355 - 6.523\,377\, x^2 + 5.819\,022\, x^4$

This trial function has no nodes other than at the end points $x = \pm 1$.
For the true eigenfunction of $n=1$ in a well of length 2 ($-1 \leq x \leq 1$), the eigenvalue is

$E = 1^2\pi^2/2^2 \bullet (\hbar^2/2M) = +2.46741 \bullet (\hbar^2/2M)$.

We found an upper bound to this energy, $E_{\text{var}} = +23.9123 \bullet (\hbar^2/2M)$.