MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.73 Quantum Mechanics I
Fall, 2018

Professor Robert W. Field

FINAL EXAMINATION

This is an open book, open note, open computer, unlimited time exam. You may talk to each other to clarify *what the questions mean*, **but not how to answer them**.

You may choose to answer either Question 2 or 3. If you have time and energy to provide some fragmentary insights into the other problem, you will receive up to 10 points *extra credit*!

Name: _____

GRADING:

    I.   _____ /60 points

    II.   _____ /40 points (or 10 points *extra credit*)

    III.   _____ /40 points (or 10 points *extra credit*)

answer one or the other

TOTAL: _____ /100 points (plus 10 points *extra credit*)

I.   Aufbau for Adults

Consider the following problems of spectrum identification and prediction.

A.   You have an absorption spectrum and you do not know whether it comes from atomic C, N, or O. You do not have access to a table of energy levels or assigned spectral lines. What are the features in the spectrum that would enable you to conclusively identify the "carrier" of the spectrum?

Here are the rules:

a.   The atom starts out in its ground electronic state. You cannot rely on any state being initially populated other than the lowest L–S–J state predicted by Hund's rules.

b.   The selection rules for electronic transitions are $\Delta\ell = \pm1$. This is consistent with $\Delta L = 0, \pm1, \Delta S = 0, \Delta J = 0, \pm1$. An off-diagonal matrix element of $\mathbf{H}^{SO}$ between same-configuration, same-J, $\Delta L = 0, \pm1, \Delta S = 0, \pm1$ states could make certain $\Delta S \neq 0$ transitions weakly observable. The intensity "borrowed" by a nominally forbidden transition is directly related to the level shifts of both the "borrowing" and "lending" state.

c.   The nuclear spins of $^{12}C, {}^{14}N, {}^{16}O$ are I = 0, 1, and 0 respectively. You can use the presence or absence of hyperfine structure to make assignments, but you must make some predictions about the qualitative nature of the hfs.

d.   You can use the Zeeman effect in a variety of ways to identify the states involved in a transition. If you do so, you must calculate g-values.

e.   The Landé interval rule should prove very helpful. If you use it, you should calculate the relative intensities of transitions to different J-components of an $S \neq 0, L \neq 0$ multiplet state. The transition intensities come from the 1-electron form of the transition operator, $T^{(1)}[\mathbf{r}]$, where $\mathbf{r}$ is the electron coordinate. This has $\Delta\ell = \pm1$ selection rules. Z-polarized light excites $\Delta m_\ell = 0$ transitions.

You should answer this question by identifying the unique spectroscopic signature of *each* of the three atoms. I am looking for quality (very specific diagnostics) rather than quantity (vague, qualitative statements).

B.   Isoelectronic and isovalent comparisons. The energy level diagrams for two
        atoms with the same number of valence electrons will resemble each other, but
        the scale parameters
        $[\varepsilon_{n\ell}, F^k, G^k, \zeta_{n\ell}]$ will be systematically and predictably different.

    (i)   How would the spectra of C^-, N, and O^+ compare? Make plausible
        arguments about how each of the scale parameters would change.

    (ii)   How would the spectra of Si, P, and S compare to the spectra of C, N, and
        O, respectively? Again, be as specific (and ingenious) as you can about
        how you expect all of the scale parameters to change.

C.   A transition from the N atom ground state to one of the ^{4}P states belonging to
        either the $2s2p^4$ or the $2s^2\,2p^2\,3s$ configuration is excited.

    (i)   How would you be able to tell to which configuration the ^{4}P state belongs?

    (ii)   The transition is excited with a 1fs light pulse. There will be quantum
        beats in the ^{4}P–^{4}S fluorescence. Be as specific as possible about the fine
        structure (J = 5/2, 3/2, 1/2) and hyperfine structure $(\vec{F} = \vec{J} + \vec{I})$
        contributions to the quantum beat spectrum. Be as specific as you can be
        about frequency ratios and the relative intensities of the various beat notes.

II.   Effective Core Potentials (Pseudopotentials)

It is often useful to simplify a many-electron problem to a one-electron problem, for example, that the active electron moves in the semi-empirically defined effective potential of the ion-core. In this problem you will use a one-dimensional ordinary differential equation solver to define $Z^{eff}(r)$ for the Ca^{2+} ^1S and Ca^+ $4s$ ^2S ions using the experimentally known quantum defects for the ns, np, and nd Rydberg series of Ca^+ and the $4sn\ell$ ^1L ($\ell=0, 1, 2$) Rydberg series of Ca.

The radial Schrodinger equation, expressed in atomic units is

$$\frac{d^2u}{dr^2} + \left[2E - 2V(r) - \frac{\ell(\ell+1)}{r^2} \right] u = 0$$

$$u(r) = rR(r).$$

E is the binding energy of the electron (the zero of energy is set at the ionization threshold)

$$V(r) = -Z^{eff}(r)/r$$

$$V_\ell(r) = V(r) + \frac{\ell(\ell+1)}{2r^2}$$

where, for Ca^+,

$$Z_+^{eff}(r) = 2 + 18(1+ar)e^{-br}, \quad a \geq 0 \text{ and } b \geq 0$$

which has the required limiting behavior

$$Z_+^{eff}(0) = 20$$
$$Z_+^{eff}(\infty) = 2.$$

The b parameter determines the overall size of the Ca^{2+} ion-core, and the a parameter permits $Z_+^{eff}(r)$ to exhibit some remnant of "shell structure." Initially, you should set a = 0 and vary b to obtain a $V_\ell(r)$ that gives the correct (i.e. empirically determined) quantum defect for the Ca^+ ns Rydberg series. After deriving an approximate value for b, you will adjust both a and b to match the quantum defects for the Ca^+ np and Ca^+ nd Rydberg series

$$E(a.u.)/hc = 2\Re = 2(109737.32\ cm^{-1})$$

$$E(Ca^{+}\ n\ell)/hc = -\frac{4\Re}{\left(n-\mu_{\ell}^{+}\right)^{2}}$$

$$\mu_{s}^{+} = 1.806$$

$$\mu_{p}^{+} = 1.454$$

$$\mu_{d}^{+} = 0.627$$

For the Ca 4s nℓ ^{1}L Rydberg series, the effective potential of the Ca^{+} 4s ^{2}S ion-core could be parametrized as

$$V_{\ell}(r) = -Z_{s}^{eff}(r)/r + \frac{\ell(\ell+1)}{2r^{2}}$$

where

$$Z_{s}^{eff}(r) = Z_{+}^{eff}(r) + (e^{-cr}-1)$$

$$Z_{s}^{eff}(0) = 20$$

$$Z_{s}^{eff}(\infty) = 1$$

This form for $Z_{s}^{eff}(r)$ treats the effect of the 4s electron as simply additive to the effective potential of Ca^{2+}. The c parameter will be much smaller than the b parameter because the radius of the 4s orbital will be much larger than that of the Ca^{2+} ion-core. Once you have optimally described $Z_{+}^{eff}(r)$ by adjusting a and b to fit the Ca^{+} nℓ Rydberg quantum defects, you should adjust c to fit the Ca 4s nℓ ^{1}L quantum defects:

$$\mu_{s} = 2.931$$

$$\mu_{p} = 1.944$$

$$\mu_{d} = 0.911$$

$$E(Ca\ 4s\ n\ell\ ^{1}L)/hc = -\frac{1\Re}{\left(n-\mu_{\ell}\right)^{2}}$$

Here is the procedure that I propose you follow. Use an Ordinary Differential Equation solver, and you MAY collaborate with each other in making the ODE solver work.

A.   Choose an initial value for the b parameter and set a = 0. You should choose the initial value of the b parameter large enough so that $Z_+^{\text{eff}}(r)$ is between 2 and 3 at $r = 9.9 \times 10^{-11}$m, which is the "official" ionic-radius of Ca^{2+}.

Solve the 1-particle radial Schrödinger equation for Ca^+ 8s. The boundary conditions are $u_\ell(0) = 0$ and $u_\ell(\infty) = 0$. You are looking for an $\ell = 0$ eigenstate with seven internal nodes. Once you find the 8s eigenstate, you need to adjust b so that the eigen-energy is

$$E_{8s} / hc = -4\Re / \left(8 - \mu_s^+\right)^2$$
$$= -438949.3 \ \text{cm}^{-1} [8 - 1.806]^{-2}$$
$$= -11441 \ \text{cm}^{-1}.$$

This will be an iterative process. Once you have found a satisfactory value for b with a = 0, repeat the iterative variation of b starting with a = 1. When you are done you will have two pairs of a,b values that give the correct energy for the Ca^+ 8s state.

Then use the two pairs of a,b values to compute the energy of the Ca^+ 8p state (six internal nodes). Both of the calculated energies are likely to be slightly incorrect. Devise (and explain) an iterative strategy so that you are able to find a pair of a,b values that gives the correct energy for both Ca^+ 8s and Ca^+ 8p.

$$E_{8p} = -4\Re \left[8 - \mu_p^+\right]^{-2}.$$

If, after ~1 hour of effort, your strategy does not yield acceptable values for Ca^+ 8s and 8p states, stop working on problem II here!

Now your $Z_+^{\text{eff}}(r)$ function should be pretty close to perfect. Test this by computing the energy of the Ca^+ 8d state (5 internal nodes).

$$E_{8d} = -4\Re \left[8 - \mu_d^+\right]^{-2}.$$

B.   (*Optional*). Now that you have determined an empirically optimized $Z_+^{\text{eff}}(r)$ for Ca^+, determine

$$Z_s^{\text{eff}}(r) = Z_+^{\text{eff}}(r) + \left(e^{-cr} - 1\right)$$

for Ca 4s $n\ell$ ($\ell = 0,1$, and 2). Optimize the c parameter in the above equation to obtain the correct energy for the Ca 4s 8s ^{1}S state,

$$E\left(Ca\ 4s\ 8s\ ^1S\right)/hc = -\Re\left[8 - \mu_s\right]^{-2}$$
$$\mu_s = 2.931.$$

Once you have done this, check this $Z_s^{\text{eff}}(r)$ function to see how well the Ca 4s 8p ^{1}P and 4s 8d ^{1}D states are predicted. If the results for 4s 8p and 4s 8d are unsatisfactory, suggest a plausible reason for the discrepancy.
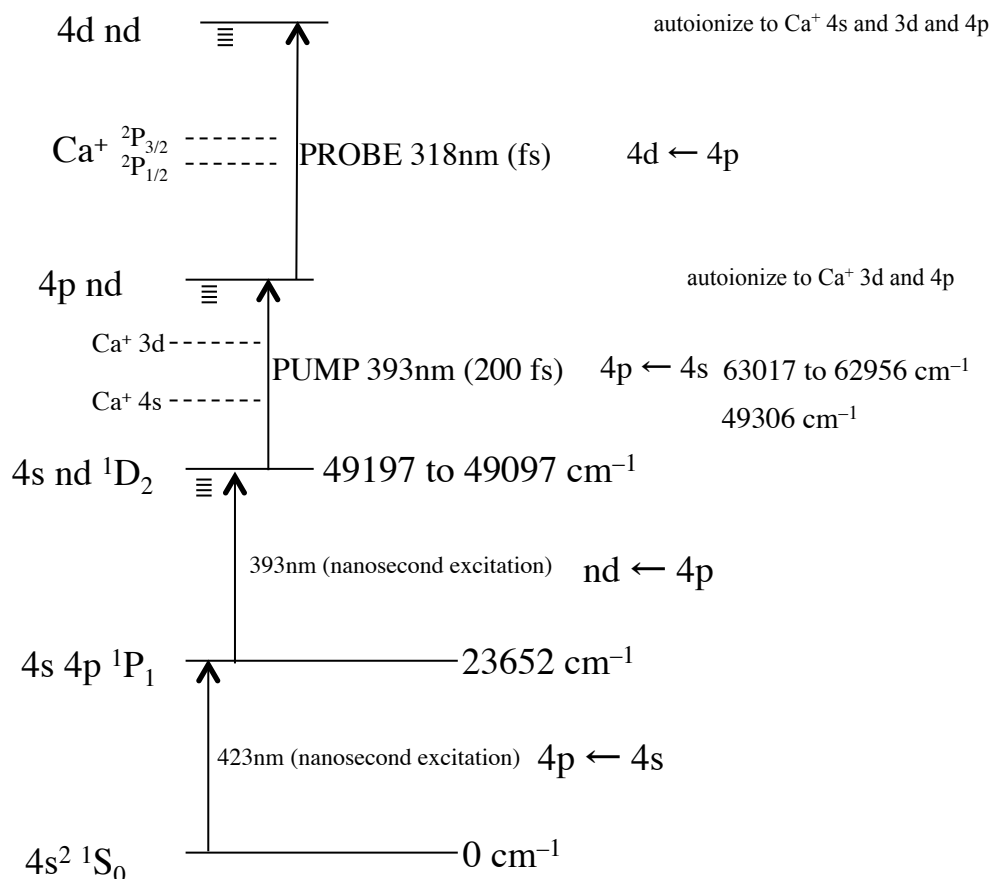
Closing comment: A similar effective core potential method could be used to find the energies of the outside-core electronic states of a charged metal solid sphere, a charged metal hollow sphere, or a charged quantum dot.

III.   Wavepacket Dynamics in Atomic Rydberg-Land.

I am going to lead you through a simplified version of the experiment described in the attached paper, "Nonexponential Decay of Autoionizing Shock Wave Packets" by Thoma and Jones [Phys. Rev. Let. **83**, 516 (1999)].

The purpose of this problem is to develop the dual skills of describing the evolution of $\Psi(t)$ as a specific linear combination of eigenstates and of describing the time–dependent pictures of wavepackets in motion. Words and concepts rather than elaborate equations will be sufficient to answer most of these questions.

The relevant energy level structure of Ca and Ca$^+$ is summarized in the level diagram:

4d nd   autoionize to Ca$^+$ 4s and 3d and 4p

Ca$^+$ $^2P_{3/2}$ / $^2P_{1/2}$ PROBE 318nm (fs)   4d ← 4p

4p nd   autoionize to Ca$^+$ 3d and 4p

Ca$^+$ 3d

PUMP 393nm (200 fs)   4p ← 4s   63017 to 62956 cm^{-1}

Ca$^+$ 4s   49306 cm^{-1}

4s nd $^1D_2$ 49197 to 49097 cm^{-1}

393nm (nanosecond excitation)   nd ← 4p

4s 4p $^1P_1$ 23652 cm^{-1}

423nm (nanosecond excitation) 4p ← 4s

4s^2 $^1S_0$ 0 cm^{-1}

Two nanosecond lasers are used to selectively populate one of several 4s nd $^1D_2$ eigenstates, in the range of $24 < n < 33$. A femtosecond laser pulse (393nm) excites the 4s electron to the 4p orbital. The frequency of this transition is expected to be very close to that of the Ca$^+$ 4p $^2P_{3/2}$ ← 4s ^2S excitation (74720 - 49306 cm^{-1} or 393nm). The spectral width of the 200fs pulse is sufficiently narrow so that 4p $^2P_{1/2}$ ← $^2S_{1/2}$ is not excited. The excitation probability for Ca$^+$ 4s ← Ca 4s nd (direct excitation of the nd electron into the ionization continuum) for the Rydberg electron is negligibly small (because of n^{-3}-scaling). The short pulse excitation causes a transition from Ca 4s 4d to a coherent superposition of Ca 4p nd eigenstates. Thus $\Psi(0)$ is a coherent superposition of quasi-eigenstates:

$$\Psi(0) = \sum_n c_n \big|4p\,nd\big\rangle.$$

These are quasi-eigenstates because they can decay by "autoionization" into the continua of Ca^+ 4s + $\varepsilon\ell$ (ℓ = odd) and Ca^+ 3d + $\varepsilon'\ell'$ (ℓ' = odd) via matrix elements of $1/r_{12}$. The energies of these $|4p\,nd\rangle$ quasi-eigenstates can be taken to be given by a simplified Rydberg formula (neglecting quantum defects):

$$E_{4p\,nd} = E\big(Ca^+ 4p\ {}^2P_{3/2}\big) - hc\,\mathfrak{R}/n^2.$$

For specificity, let $32 \le n \le 37$ (six states) and let $|C_n|$ be $6^{-1/2}$ for all six n values. The 200fs 393 nm PUMP pulse launches a wavepacket that, at t = 0, is identical to the nd orbital in the $|4s\,nd\rangle$ initial eigenstate. The outer lobe of this wavefunction is located near (but not at) the outer turning point of the $|4p\,nd\rangle$ quasi-eigenstates. The wavepacket will evolve in a way that you will need to figure out. The oscillation period is called the Kepler period. Note that if you choose wavefunction phases so that the innermost lobe is always positive, the outermost lobe will exhibit a phase that oscillates with principal quantum number, in this case $(-1)^n$.

A.   For the $32 \le n \le 37$ wavepacket, what is the Kepler period, T_k?

At different times during a Kepler period the way in which the wavepacket created by the 393nm 200fs PUMP pulse is affected by the 318nm 200fs PROBE pulse changes. The PROBE pulse acts on the inner (4p) electron. The 4d $\leftarrow$ 4p transition amplitudes from all of the quasi-eigenstate components are in phase when the wavepacket has returned to its original form at t = 0, T_k, $2T_k$ and mostly out-of-phase at t = $T_k/2$, $3T_k/2$, …

B.   For the $32 \le n \le 37$ wavepacket at t = $T_k/2$, describe the time-dependent amplitude of each of the quasi-eigenstate n-components in $\Psi(T_k/2)$. Be explicit about the phases of the innermost and outermost lobes of each n-component.

When the initially created wavepacket is at its t = 0, T_k, $2T_k$ form, its rate of autoionization into the Ca^+ 4s + $\varepsilon\ell$ (ℓ = odd) and Ca^+ 3d + $\varepsilon'\ell'$ (ℓ' = odd) continua will be different from when it is at its t = $T_k/2$, … form. $\varepsilon\ell$ is the kinetic energy of the ejected ℓ electron. Figure 2 of the attached paper suggests that the autoionization rate is minimized at t = 0, T_k, $2T_k$ and reaches one or two maxima during each Kepler period. The autoionization is due to matrix elements of $1/r_{12}$. The inner part of the nd Rydberg orbitals is most important in determining the magnitude (scaling as $n^{-3/2}$) of $\big\langle 4p\,nd\big|1/r_{12}\big|3d\ \varepsilon'\ell'\big\rangle$ and $\big\langle 4p\,nd\big|1/r_{12}\big|4s\ \varepsilon\ell\big\rangle$ matrix elements.

C.   Explain the oscillations in the autoionization rate of the 4p nd wavepacket. I will be very impressed by an explanation that accounts for the two maxima in the autoionization rate during each Kepler period.

The 318nm 200fs PROBE pulse excites 4d n'd ← 4p nd [via Ca^+ 4d ← 4p] (the quantum defects for the 4d n'd and 4p nd quasi-eigenstates are slightly different). This new wavepacket also autoionizes. The autoionization signals due to the PUMP by itself and the PUMP + PROBE are distinguished via the kinetic energy of the ejected electrons, so the systematically time-delayed PROBE pulse is capable of sampling the population in the PUMP-produced $\Psi(t)$, with approximately 400fs time resolution.

If there were no autoionization from the PUMP-produced wavepacket, there might still be a delay-time dependence of the PROBE-induced excitation probability.

D.   Derive an expression for the delay-dependent PROBE excitation rate. *Explain your assumptions* in deciding whether the excitation rate is maximal at:
  (i) $t = 0, T_k, 2T_k$ or
  (ii) at $t = T_k/2, 3T_k/2, \ldots$ or
  (iii) independent of t.
This is related to your answer to part **B**.

The article on Pages 11–14 has been removed due to copyright restrictions. See Thoma, J.E. and R.R. Jones. "Nonexponential Decay of Autoionizing Shock Wave Packets." *Physical Review Letters*. **83** (1999): 516–519.

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