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Progress Report

Improved Calculation of Two-photon opacity

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OUTLINE

1.) Overview
    - Two-photon code began with a 1-page "hand calculation"
    - Now added all the BF and FF parts and it is a 150 page Fortran program
    - Now includes 44 ions (charge and excitation states) of Fe 14^+ to 19^+.
    - Disagrees with Kruse-Iglesias calculation

2.) Advantages of new code structure
    - Can change radiation spectrum
    - Can change the elements and ions
    - Parts of the opacity can be separated: Raman, BB and BF, RR, RLLR chains
    - MGM cross-section to compare to future X-FEL experiments and other researchers.
    - Angular distribution of X-rays can be important.
        - The code provides cross-sections for 3 cases: isotropic, anisotropic and XRL beams.

3.) Free-free matrix-elements and divergent integrals for free states
    - Several years' work on this mathematics is now installed.

4.) Which ions are important in the 7-10 A range?
    - SAM AA and DCA calculation
        - Generate ions by nested loops
        - Energies from SC model   similar to SBH & DAL
    - Each ion is described by a set of eigenvalues $\varepsilon_{n,l}$
    - Excited state energies are obtained from the eigenvalues,
    - This method omits term-splitting
    - 44 ions included in latest 2-phot run
        - Form opacity *per ion* before averaging over thermal populations
        - This gives a fair comparison of which ion is important in the thermal mix.
        - Often, it is an excited state related to a higher-charge ion.
    - Certain ions are especially important (for the 7 - 10 A range).
    - Continuum lowering effect
    - Plans for further analysis

Appendix A: Hand calculation
Appendix B: Handling the $1/(x-x_o)$ integral   (Simpson + correction)
Appendix C: Controls for the continuum integration
List of Ions included ("IONLIST")

This report was prepared for task 6 described in Sandia Purchase Order **1925681** mod 2:

Task 6.) Perform further refinements in the code using the perturbation approach to two-photon opacity calculations. These refinements will include ability to more accurately treat free-free matrix elements and plasma density effects. The ability to accept an arbitrary input radiation spectrum will be provided. The structure of the code will be altered to enable more rapid switching from one element to another.

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1.) Overview

This report will describe an improved computer code for two-photon opacity. The new code incorporates many recent advances and is ready to start to face the experiments. It incorporates the difficult mathematical techniques for handling free states and free-free matrix elements.

The new code grew out of the "hand calculation" described in a recent paper submitted to HEDP (details in Appendix A). The original version evaluated the second-order perturbation theory formula for the MGM two-color cross-section for bound states $n=1$ to $n=5$ (all l-values). The calculation was small enough to be done on a pocket calculator. It could be compared to the AC Stark code (time-dependent Schroedinger equation) for Fe ion in applied X-ray fields, described by Gaussian wave-packets. Using the same atomic data, the two methods agreed to a few percent.

New features in today's code are the bound-free and free-free matrix-elements and a sum over many initial states (charge states and excitation states) and final states. The code is now a 150 page FORTRAN program. Details are given in this report. Some sample results are attached.

The results definitely disagree with a recent paper of Kruse and Iglesias. Those authors argue that Raman effects are not important, maybe misunderstanding the relation between Stokes and anti-Stokes Raman transitions. Kruse and Iglesias apparently calculated only one case --- absorption by 2s electrons in ground-state Neon-like Fe ions --- and found a small two-photon absorption cross-section. Instead we combine calculations for *many cases*, some 20 to 25 bound-bound transitions for each of 44 ions plus a large number of bound-free transitions to the continuum. For the case they calculated (Ne-like 2s absorption), we also find a small answer. Among the *many thousand other cases,* we find some large cross-sections and the average opacity on the 7-10 Angstrom range is (with today's calculation) 125 cm^2/gram, about a hundred times larger than their result. However it is not clear whether it will be large enough to explain the extra opacity seen in the Sandia Z-machine experiments. Some of our largest cross-sections come from the Raman (Stokes) absorption. We also find some narrow absorption features that may disagree with experiment. These features might be smoothed by term-splitting or might move out of the 7-10 A range if calculated with more accurate excited-state energy levels.

2.) Advantages of new code structure

The new code was written to a plan that offers several advantages.

a.) Can easily change radiation spectrum. This may be important for comparison to Laboratory experiments because, for example, an excess of hard photons (as compared to a black-body flux) can change the population of high-charge ions or highly excited states.

b.) Can change the elements and ions. The code stores the atomic energy data for each ion in a separate subroutine. These 44 subroutines have a standardized format and can easily be separated from the code or replaced. Each subroutine describes the initial (lower) state for an absorption transition. The atomic data in the subroutine is the overall binding energy, statistical weight and a set of excited-state eigenvalues. The data comes from a relativistic semiclassical self-consistent field code ("SAM") but could be replaced by data from other sources. The binding energy and statistical weight are used to assign Boltzmann population probabilities for the different ions. Changing to another material only requires a certain amount of typing and copying.

A future version of this code can combine these data subroutines in a big file separate from the opacity code to make it easier to switch data-sets. Attached plots of energy levels for excited states Fe 17^+ and 18^+ ions are already made by this method.

c.) Parts of the opacity are printed separately so they are easy to compare.

The opacity can be divided up into Raman and non-Raman absorption parts, into bound-bound (BB) and two-photon photoelectric (BF) parts, and into contributions from RR and RLLR chains. A typical RR absorption is *2s --> n_1p --> n_2d*, summed over n_1. A typical RLLR chain would be transitions *2p --> n_2p,* which can go through intermediate states n_1*s* or n_1*d*. These *s*- and *d*- chains run between one definite initial state and one definite final state so they can interfere.

The code prints the pieces of the total opacity separately so they can be compared. Especially when we consider absorption over a specific photon wavelength window (e.g., *7 - 10 A*) some pieces are large and some are small.

The code calculates the MGM two-color cross-section. That cross-section ($cm^4 eV$ units) can be compared to calculations by other people, such as J. Colgan & M. Pindzola or T. Rescigno and his collaborators. Future X-Ray Free-electron Laser experiments will also measure the MGM cross-section. In our code the MGM cross-section is integrated over the energy distribution of the second photon to predict attenuation (opacity) for the "first" photon.

d.) The X-ray angular distribution can be important. Two-photon cross-sections are of interest for three physical situations:

i.) Near-LTE radiation transport, as inside stars,

ii.) Laboratory experiments on samples heated by an external radiation source, as in the Z experiment or in future backlight-heated laser opacity experiments,

iii.) Samples irradiated by intense X-ray laser beams (X-FEL experiments).

If the x-ray wavelength is enough larger than the atomic size (a few Angstroms) the only dependence on the angular distribution is through the polarization vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ of the two x-rays. The theoretical cross-section is predicted to depend on these vectors as:

$$\sigma = \sigma_0 + \sigma_1 (\boldsymbol{e}_1 \bullet \boldsymbol{e}_2)^2$$

Our code provides the two numbers, σ_0 and σ_1. Usually we combine these with assumed values for the average dot-product of polarization vectors $< (\boldsymbol{e}_1 \bullet \boldsymbol{e}_2)^2 >$.

3.) Free-free matrix-elements and divergent integrals for free states.

Several years' work on this mathematics is now completed and installed. The straightforward calculation of two-photon opacity involves an integral whose integrand tends to infinity at three energies. Such an integral is not necessarily infinite but is certainly troublesome. It requires careful mathematical analysis to extract a unique "correct" value from the formulas. We outline that analysis here and give details in Appendices B and C.

The basic formula for the MGM cross-section can be written

$$\sigma^{MGM}(h\nu_1, h\nu_2) = \frac{8\pi\alpha^2\hbar}{g_i h\nu_1 h\nu_2} \left| \sum_j \left(\frac{\delta E_{ij}\hat{e}_1 \cdot \vec{R}_{ij} \;\; \delta E_{jk}\hat{e}_2 \cdot \vec{R}_{jk}}{E_i + h\nu_1 - E_j} + \frac{\delta E_{ij}\hat{e}_2 \cdot \vec{R}_{ij} \;\; \delta E_{jk}\hat{e}_1 \cdot \vec{R}_{jk}}{E_i + h\nu_2 - E_j} \right) \right|^2 n(h\nu_1) \;\; n(h\nu_2)$$

This formula is already condensed. The fine-structure constant is $\alpha = e^2/\hbar c$; g_i is the statistical weight of the initial state, *j* labels an intermediate state (bound or free), the δE's in the numerator are energy-differences between the states involved in the matrix-elements ***R***. In the formula the ***R***'s are vectors but they can easily be separated into radial and angular parts. E_i is the energy of the initial state, $h\nu_1$ and $h\nu_2$ are the energies of the two photons, E_j is the intermediate state energy. The two terms occur because the two photons can be absorbed in either order.

The averaging over the photon polarization vectors, $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$, is important but we do not discuss it here. The formula is an amplitude squared times pre-factors and post-factors. The post-factors ("n_1, n_2") are photon populations (Planck functions) and were discussed in previous reports. The pre-factors come from time-dependent perturbation theory and from the electron-photon coupling Hamiltonian. They are all just numbers. The difficulty is with the sum (= integral) inside the absolute value signs.

This is a sum over intermediate states: the atom goes from a (determined) initial state "*i*" to a definite final state "*k*" through a mixture of intermediate states "*j*". Those different possible intermediate states all exist simultaneously and the various possibilities interfere. That is why the numbers are added *before* the absolute square is taken.

The sum over intermediate states can be a discrete sum over bound states (typically 5 states are possible for a transition like *2s --> np --> 6d*) or it can be an integral over positive energy states, *E"p* in the *2s --> 6d* case. The final state can also be a free state and in that case, the most difficult case, the intermediate state sum again requires an integral.

The basic method of integration we adopt is Simpson's rule, a textbook mathematical technique. The interesting cases require modification of Simpson's method for the special energy-ranges where the integrand is diverging. For Simpson's rule, we have a grid of equally spaced (positive) energies for the free electron states. Denoting these energies as x_i, Simpson's rule says

$$\int g(x)\ dx \ = \sum_{even\, i} \frac{dx}{3}\left[g(x_{i-1})+4g(x_i)+g(x_{i+1})\right]$$

Alternate values of $g(x)$ are weighted by *2/3* and *4/3* and this weighting makes a compensation for smooth variations of $g(x)$ with x. The formula is exact for locally quadratic functions $g(x)$.

When this formula is used for the amplitude of the two-photon absorption, the integrand g(x) has the form

$$g(x) \ = \ \frac{f(x)}{x-x_o}$$

where $f(x)$ is the combination of energies and matrix-elements in the numerator and $x - x_o$ is the energy denominator.

The integrand can become infinite in three ways. They may not all happen but the code must be ready if they do. One way is if the intermediate free energy equals the final free energy. At that point, the numerator $f(x)$ is infinite because one of the matrix-elements in the $f(x)$ diverges. The other two ways occur if the denominators are zero (i.e., $x = x_o$). Those are easier to handle.

For the first difficult case (intermediate free energy = final free energy) the solution was described in detail in the paper we recently submitted to the HEDP journal. The method was tested by a matrix version of the f-sum rule for positive energies. The matrix-elements and the method of handling their singularity satisfied the f-sum rule to very nice accuracy. In fact that test is more delicate (numerically) than the opacity calculation, so the part-per-million accuracy needed there may not be needed for the opacity.

The integrals are also singular if the energy denominators vanish. That could occur for two intermediate state energies. Although the singularity could be truncated by introducing a lifetime for the intermediate state, it is possible to evaluate the principal value of the integral by making a power-series expansion near the divergence. That seems to be the most reliable way to handle the divergence. Appendix B gives the formulas. The three singular possibilities might occur in either order and might even (hypothetically) overlap. Appendix C describes how to control the calculation to deal with whatever case might occur.

4.) Which ions are important for the 7-10 A range?

The calculation we perform uses a basis set of states with decided configurations but without the term splitting. This is a version of the "super-configuration" method, in which the states with a specified occupation of the one-electron *n,l* states are grouped together. The states discussed here are the lower (initial) states for absorption. A typical case is the ion #20 on our list, which has configuration $1s^2\ 2s^1\ 2p^4\ 3s$. It is an excited state of the 18^+ ion, excited relative to the $1s^2\ 2s^2\ 2p^4$ ground-state of that ion. The calculated LTE probability of finding ion # 20 is *0.416%*. The ion can absorb by transitions of its *2s, 2p* or *3s* electrons. The code sums over all these possibilities. The energy after the absorption is calculated using the eigenvalues $E_{n,l}$ for ion 20. These eigenvalues are stored in a data base. To make the opacity, the contribution from ion 20 is weighted by .00416 in the sum over ions.

The energies for these excited states, and the LTE partition function that determines their probabilities are calculated by a relativistic semiclassical computer code called SAM. This code has been described in conference proceedings but was never published or released for other people to use. The relativistic WKB method was described in a paper published in 1994, cited below.

The SAM code calculates an "average atom" model using Fermi statistics for the electron populations, but also performs a "detailed configuration" calculation using integer populations for a large number of excited states (each state is defined by the configuration $\{P_{nl}\}$ where the *P*'s are integers). This method is an approximate brute-force treatment of the many-body problem, because the electron-electron interaction is included in the self-consistent potentials for each ion. The energies are approximate but, for example, the ionization potentials are accurate to a few percent.

It is interesting that the AA and DCA (Saha) calculations obtain slightly different answers, even using the same atomic energies. For the AA calculation, $Z^* = 16.671$ at density $\rho = 0.157\ g/cm^3$ and $kT = 190\ eV$. The detailed configuration (Saha) calculation for the same density and temperature found $Z^* = 17.321$. Is that difference significant? Is it a measure of the uncertainty in these (LTE) calculations? From a fundamental point of view, the AA model uses Fermi statistics for the electron populations but Fermi statistics describes non-interacting electrons. For this case we have an exact Saha calculation to compare to the AA method.

For the Fe ions at $T = 190\ eV$, some *233,380* configurations were considered. They are generated systematically by nested do-loops which assign $P_{2s} = 0,1,2$, $P_{3p1/2} = 0,1,2$, $P_{3p3/2} = 0,1,2,3,4$ and so forth. The K-shell population P_{1s} is kept frozen at 2 because it would require too much energy to change. The one-electron energies have relativistic splitting so $2p_{1/2}$ and $2p_{3/2}$ states are distinguished. The relativistic effects are not large for Fe ions but might be important for heavier atoms. For higher shells ($3d_{5/2}$ to $4d_{5/2}$ states) the populations considered are only 0 and 1. The total number of configurations considered is thus 1 for the K-shell, 45 for the L-shell, 162 for the M-shell and 32 for the N-shell.

For these states (233,380 configurations) the energy and statistical weight are combined using Boltzmann statistics to form the thermal equilibrium populations. The charge state for each case is determined from the populations and the total probabilities for each charge state is calculated.

The high-charge ions are mainly in their ground-states but the lower charge ions are often in excited states. This behavior is measured by the partition function, a sum over excited states for each charge-state. A comparison of ion populations with numbers calculated by a different method by S. B. Hansen showed qualitative agreement.

Many of the ions and excited states have small populations. We have chosen a finite set (44 ions) to use as lower levels in the two-photon absorption calculation. We began with ground-state ions of Z* = 14 through 19; these have the highest probabilities. After that we selected excited states, in a semi-logical way, until we had exhausted ~ 96 % of the total probability. The ion densities or probabilities of the states we selected can be unambiguously decided because we know the overall partition function and the excitation energy and statistical weight of each state in our list. (The list is copied below.) This list may further evolve in the near future because the accounting is not yet perfectly systematic. We probably do not include enough excited states of the low-charge ions.

An advantage of the SAM code is that we can easily generate a similar data-set for other elements. We will be a little more systematic in selecting the states and might be better organized for filling the data-base system.

The two-photon opacity calculation cycles through the list of 44 ions. It considers *2s, 2p, 3s, 3p* and *3d* electrons for each ion, and allows them to absorb two photons in the various allowed ways. For example, the *2p* electron can absorb to *4f, 5f, 6f* and *7f* states and also to *3p, 4p, 5p, 6p* and *7p* states. Transitions to free states are also considered (2p --> *E,f* and *E,p* states with *E > 0*) and integrated over. Certain of the transitions are especially important for the 7 - 10 A range.

We are nervous when any change in the computational model makes a significant change in the predicted opacity. However when we are considering opacity on a finite range such as *7 - 10 A*, the total can change if the energy-levels change enough to shift a strong transition out or into that wavelength range. When the energy levels change (either by considering different ions or different basic atomic models), such changes are inevitable.

At present, the theory neglects term splitting. Term splitting is expected to be a rather strong effect. For example, an ion with a partly-filled *2p* shell should split into several terms split by as much as *30-60 eV*. The total absorption strength from the split terms is likely unchanged but if one absorption feature splits into three, that splitting will smooth the results.

Since there are so many ions in our mixture, it seems impractical to calculate the effect of term splitting for each one. However, since we know which ions are most important for the two-photon opacity, we can estimate the term-splitting effect for at least the most important few.

Finally we revert to the most important question: what makes certain ions, and certain transitions most important for the 7 - 10 A range? The photon $h\nu_1$ in this range does not generally match a difference of ion energy-levels. However if the second photon absorbed with it matches the difference of two bound-state energies, that coincidence seems to enhance the cross-section, sometimes very strongly. If there is such a coincidence for a 17^+ ion, we can search for a related state among the 16^+ ions that has the same core populations plus one extra outer electron. That 16^+ ion is a good candidate for a similar large cross-section. This analysis has not been carried through sufficiently carefully so we expect increases in the predicted opacity.

Changing the continuum lowering model has also raised the opacity in our recent calculations. The SAM code assigned a single fixed ion-sphere continuum lowering (shift of all energy levels) based on the charge state (~ 16.6) of the average-atom. We removed this and found a higher opacity. A better model will assign each ion an appropriate CL, different for different ions, calculated from the free-electron density and the ion's charge.

It should be clear from this discussion that there are a number of things to try. Generally they are aimed at getting an opacity more like the experimental numbers, but we cannot guarantee that will be possible. We will explore the temperature dependence of the results and will look for possible special effects of a radiation spectrum having more high-energy photons than a Planck function would assign. The progress reported here is that the code is ready to try these experiments. Of course in doing that we will constantly check the code logic and mathematics to be sure the calculation performed is what it should be.

One useful thing to test is to increase the frequency resolution to see what is the width of the narrow absorption features in the opacity. That change might increase (or reduce) the average opacity.

Reference:
"Relativistic Semiclassical Atomic Transition Rates," R. More, J.Q.S.R.T. **51**, 237 (1994).

APPENDIX A.) Hand calculation

This appendix describes a *hand calculation* using the two-photon perturbation theory formula to compare to the AC Stark code. (The text of this appendix is only slightly modified from the paper we have submitted for publication in HEDP and is copied here for convenience.) The hand calculation uses the *same* states, energies and matrix-elements as the solution of the time-dependent Schroedinger equation. The time and frequency ranges used for that time-dependent calculation affect the inferred cross-sections as described in the HEDP paper. With the hand calculation there is no issue of integration time or spectral widths. (The "hand calculation" uses a pocket calculator!)

The hand calculation has been installed in a one-page computer code, the "Bridge" code. It was then extended by adding matrix-elements and energy levels and is the basis of our present best computer code. (The current name is "Pontcinq" which evolved from the name "Bridge".)

Atomic data used in the AC Stark code includes one-electron energy levels for the Fe^{16+} ion:

E_{1s} = - 7,561 eV
E_{2s} = - 1,348.1 E_{2p} = - 1,256.4
E_{3s} = - 464.56 E_{3p} = - 435.25 E_{3d} = - 394.84
E_{4s} = - 203.39 E_{4p} = - 191.43 E_{4d} = - 175.82 E_{4f} = - 166.24
E_{5s} = - 93.654 E_{5p} = - 87.755 E_{5d} = - 80.119 E_{5f} = - 75.210 E_{5g} = - 72.549

The hydrogen matrix elements (atomic units) are:

$R_{2s}{}^{2p}$ = - 5.196152
$R_{2s}{}^{3p}$ = 3.064815
$R_{2s}{}^{4p}$ = 1.282277
$R_{2s}{}^{5p}$ = 0.773952
$R_{3s}{}^{2p}$ = 0.938404

$R_{2p}{}^{4d}$ = 1.709702
$R_{3p}{}^{4d}$ = 7.565411
$R_{4p}{}^{4d}$ = -20.784610
$R_{5p}{}^{4d}$ = 3.045320
$R_{2p}{}^{3d}$ = 4.747992

$R_{3s}{}^{3p}$ = -12.727922
$R_{3p}{}^{3d}$ = -10.062306
$R_{3s}{}^{4p}$ = 5.469336
$R_{4p}{}^{3d}$ = 1.302254
$R_{3s}{}^{5p}$ = 2.259575
$R_{5p}{}^{3d}$ = 0.482798

These BB matrix-elements are multiplied by a_o/Z^*, where $a_o = .529177\ 10^{-8}\ cm$ and $Z^* = 16$ for Ne-like Fe. The matrix elements can be checked against formulas from the Bethe-Salpeter book and agree nicely, except for the sign of the $\Delta n = 0$ transitions.

The angular factor for absorption *s-p-d* is $\Gamma_{ang} = .088889$ when the two photons have the same polarization. If the polarizations are perpendicular, $\Gamma_{ang} = .06666$.

The formula from second-order perturbation theory is

$$\sigma^{MGM}(\hbar\omega_1,\ \hbar\omega_2) = \frac{8\pi^3\alpha^2\hbar}{(\hbar\omega_1)(\hbar\omega_2)(2l+1)} \left| \sum_n \frac{\delta E_{in} R_{in} \delta E_{nf} R_{nf}}{E_i - E_n} \right|^2 \Gamma_{ang}\ I(\hbar\omega_1 + \ \hbar\omega_2)$$

The line-profile function $I(\hbar\omega)$ is an energy-conserving delta function so the sum of photon energies should equal the energy difference of upper and lower level. The symbol "n" above represents the intermediate state including the photon(s) present.

We consider the case *2s --> np --> 4d* and include states n = 2, 3, 4, 5 as does the AC Stark code. For detuning by $\Delta E = 50$ eV from "resonance", i.e., at $\hbar\omega_1 = 962.85$ eV, $\hbar\omega_2 = 209.43$ eV, the formula gives a cross-section of $\boldsymbol{4.3726\ 10^{-52}\ cm^4 sec\text{-}eV}$ (this is an MGM cross-section per 2s electron, integrated across the absorption profile). The cross-section is accurately proportional to $1/\Delta E^2$, for moderate values of $\Delta E \leq 50$ eV. At different photon energies, different intermediate states are most important. As written above the MGM cross-section has both photon energies specified.

It should be clear these are not final predictions of the opacity because many other initial, final and intermediate states must be included to predict the opacity. The opacity cross-section is the integral of σ^{MGM} over the photon spectrum for $\hbar\omega_2$ and that will give a much larger answer. The benefit of this calculation is that the comparison to the time-dependent Schroedinger equation (AC Stark code) verifies the handling of intermediate states (the two-photon orders), signs and other details of the perturbation theory calculation. That is a powerful mutual verification of the two methods of calculation.

Appendix B: handling the singular integral of *f(x)/(x-xo)*

Opacity calculations by perturbation theory use the formula

$$\sigma^{MGM} = \frac{8\pi^3\alpha^2\hbar}{g_i h\nu_1 h\nu_2} \left| \sum_j \left(\frac{\delta E_{ij}\hat{e}_1 \cdot \vec{R}_{ij}\ \ \delta E_{jk}\hat{e}_2 \cdot \vec{R}_{jk}}{E_i + h\nu_1 - E_j} + \frac{\delta E_{ij}\hat{e}_2 \cdot \vec{R}_{ij}\ \ \delta E_{jk}\hat{e}_1 \cdot \vec{R}_{jk}}{E_i + h\nu_2 - E_j} \right) \right|^2 n(h\nu_1)\ n(h\nu_2)$$

In some cases the results were too large to believe.

The big results occur when the integrand is infinite. For free intermediate states the sum over j is an integral over the intermediate energy E_j. Even if the integral is not infinite, most methods of integration need to be "fixed up" when the integrand gets infinite. There are two or three ways the integrand can be infinite. The difficult way is when a matrix-element in the numerator (R_{jk} above) gets infinite. That happens when the intermediate state j has the same energy as the final state k. The solution to that divergence is the long story about free-free matrix-elements and corrector functions U(E), V(E). That fix, described in detail in the paper submitted to HEDP, is now in the code and seems to work properly.

The easier difficulty occurs when one of the two explicit energy denominators is zero. There are two terms because photon 1 could be absorbed first (first term above) or photon 2 could be absorbed first (second term). Those possibilities can interfere, which is why the amplitudes are added before being squared.

The solution for this is messy but not difficult. There are some test cases where the exact answer for that type of integral is known and they can be used to check the numerical method.

The code has many zones (tens of thousands) for the intermediate free states and the integral takes them two-at-a-time, using Simpson's rule. For the $R \to \infty$ problem, the *U, V* fix just replaces Simpson's rule on one step (i.e., on two zones in E-space). To use the algebra from the HEDP paper, we require the final state energy to fall exactly on the center of one of the groups of three used for Simpson's rule. This constraint is no problem.

However, the correction for a vanishing denominator needs to work with at least six *E*-zones to calculate the integral. There is one such correction when the denominator d_{12} is zero and another one when d_{32} is zero. When the d_{12} piece is zero, the d_{21} integral for that batch of zones is still done by the normal Simpson rule. This is a control problem. We must worry about overlapping corrections.

To correct for the vanishing denominator, the numerical method is to make a power series expansion around the singular point (where one denominator vanishes). Here I sketch the math, writing "*x*" for the energy variable, which is called E_j above.

The goal is to evaluate a singular integral $I(x_o)$ of the form:

$$I(x_0) = \int \frac{f(x)}{x - x_0} dx$$

We want the "Cauchy principal value" of the integral. We could get that if we chose integration points located symmetrically above and below x_0 because the large plus and large minus values near x_0 might cancel to some accuracy.

There's a better method, analytic integration, which makes a power series for $f(x)$ around x_0 :

$$f(x) = f(x_0) + (x - x_0) f'(x_0) + \tfrac{1}{2}(x - x_0)^2 f''(x_0)$$

Then the integral of the $f(x_0)$ term will give a logarithmic piece which is not infinite and the other terms are easy.

The code calculates the numerator $f(x)$ on a grid of equally spaced energy values x_i but the quantity x_0 does not have any special relation to the x_i's. This means we need a flexible interpolation method. If x_o falls close to the endpoint of a range, the large values from $1/(x - x_o)$ might contaminate the integral over the next group of zones, so we will correct neighbor zones for a total of six zones. First we must find the coefficients in the power series, $f(x_0)$, $f'(x_0)$ *and* $f''(x_0)$.

We know the function $f(x)$ on the original grid, i.e., $f(x_{i-1})$, $f(x_i)$, $f(x_{i+1})$. The x_i's are equally spaced so $x_{i+1} - x_i = x_i - x_{i-1} = \Delta x$. Straightforward but lengthy algebra relates the coefficients to the known function values. The result of the algebra is

$$f''(x_0) = \frac{f(x_{i+1}) - 2f(x_i) + f(x_{i-1})}{\Delta x^2}$$

$$f'(x_0) \;=\; \left(1-\frac{2(x_i-x_0)}{\Delta x}\right)\frac{f(x_{i+1})}{2\Delta x}+\frac{2(x_i-x_0)}{\Delta x^2}f(x_i)-\left(1+\frac{2(x_i-x_0)}{\Delta x}\right)\frac{f(x_{i-1})}{2\Delta x}$$

$$f(x_0) \;=\; \left(-\frac{(x_i-x_0)}{2\Delta x}+\frac{(x_i-x_0)^2}{2\Delta x^2}\right)f(x_{i+1})+\left(1-\frac{(x_i-x_0)^2}{\Delta x^2}\right)f(x_i)+\left(\frac{(x_i-x_0)}{2\Delta x}+\frac{(x_i-x_0)^2}{2\Delta x^2}\right)f(x_{i-1})$$

One quick check of the algebra is to examine the special case $x_0 = x_i$. A second check is obtained by substituting $x_0 = x_i \pm \Delta x$. A more elaborate check is to show that these formulas are exact for any quadratic function $f(x)$, but that is actually already implied by the first three tests.

That is the method for the case where one denominator vanishes. The method will alter the Simpson-rule calculation for seven of the original energy values = three of the Simpson-rule steps = six of the energy intervals.

------- x_{i-3} ---- x_{i-2} ---- x_{i-1} ---- x_i ---- x_{i+1} ---- x_{i+2} ---- x_{i+3} ----

(<--------------->)

The singularity point x_0 happens somewhere in the smaller range $(x_{i-1}\,,\, x_{i+1})$ but, ahead of time, we do not know where. It might occur close to x_{i+1} and if so it will reduce the accuracy for the next group of zones. The method of calculation should be ok for any location of x_0. Then the integral of the first term of the power series is

$$f(x_0)\;\log\left(\frac{x_{i+3}-x_0}{x_0-x_{i-3}}\right)$$

This replaces the three Simpson-rule expressions for zones centered on x_{i-2}, x_i *and* x_{i+2}. The other two terms of the power-series are not difficult, but they are also integrated from x_{i-3} to x_{i+3}.

Readers who are skilled with this sort of math may want to ask about the sign of the quantities inside the logarithm. The answer to that question is a little wordy and we invite the question for our next visit to Sandia.

Appendix C: Controls for the continuum integration

We use instruction flags to tell the code what to do in several different possible (imaginable) cases.

case **a**.) In the "normal" case where there is nothing singular in the energy range considered or nearby. Then we just use Simpson's rule.

case **b**.) This is the "U, V" singularity where the intermediate state energy E'' is equal to the final state energy. (I called this E'' different names above: the first formula called it E_j and just above it was x_0.) Since the final energy is known, E'' is not hard to find. In this case, the *U, V* correctors are used for both the d_{12} and d_{21} parts of the integral (Simpson's rule is not used for this zone).

case **c**.) The denominator d_{12} could be zero, $d_{12} = E_i + h\nu_1 - E'' = 0$ which occurs when

$$E'' = E_i + h\nu_1$$

E_i is the initial state energy. In this case the treatment is to handle the diverging d_{12} integral by the power-series method of Appendix B and the other term (the d_{21} term) by the normal Simpson rule.

case **d**.) The other denominator d_{21} could be zero which occurs when

$$E'' = E_i + h\nu_2$$

For this case the d_{21} part is handled by the method of Appendix B and the d_{12} part by Simpson's rule. Notice that this change (as in case c) affects 6 zones of column while the parallel zones of the other denominator are not affected.

case **e**.) Could both **c** and **d** happen? If that occurs, the two photons have the same energy and

$$h\nu_1 = h\nu_2 = (E_f - E_i)/2 \qquad E'' = (E_f + E_i)/2$$

This is "no problem" because the fixes for the d_{12} and d_{21} channels are independent and do not interfere with each other.

case **f**.) To get both **b** and **c** to happen, we'd need

$$E'' = E_f \qquad \text{and} \qquad E'' = E_i + h\nu_1$$

This will give zero for the attenuation opacity because those two equations require $h\nu_2 = 0$. (The attenuation opacity has a factor $(h\nu_2)^2$ from the photon flux.)

case **g**.) To get both **b** and **d** to happen, it would be necessary that $h\nu_1$ be zero. We do not even try to calculate that, $h\nu_1$ is an X-ray energy.

case **h**.) It's not possible to get all three problems (b, c, d) at the same time. The equations conflict.

How to control the integration? It's turned out to be easy. We set up a pointer variable that is preset for each zone of the energy integral. It has the information to recognize which case is occurring and it sends the calculation to the appropriate instructions. It's possible to preset the pointer because we have simple equations (given above) that identify the different cases.

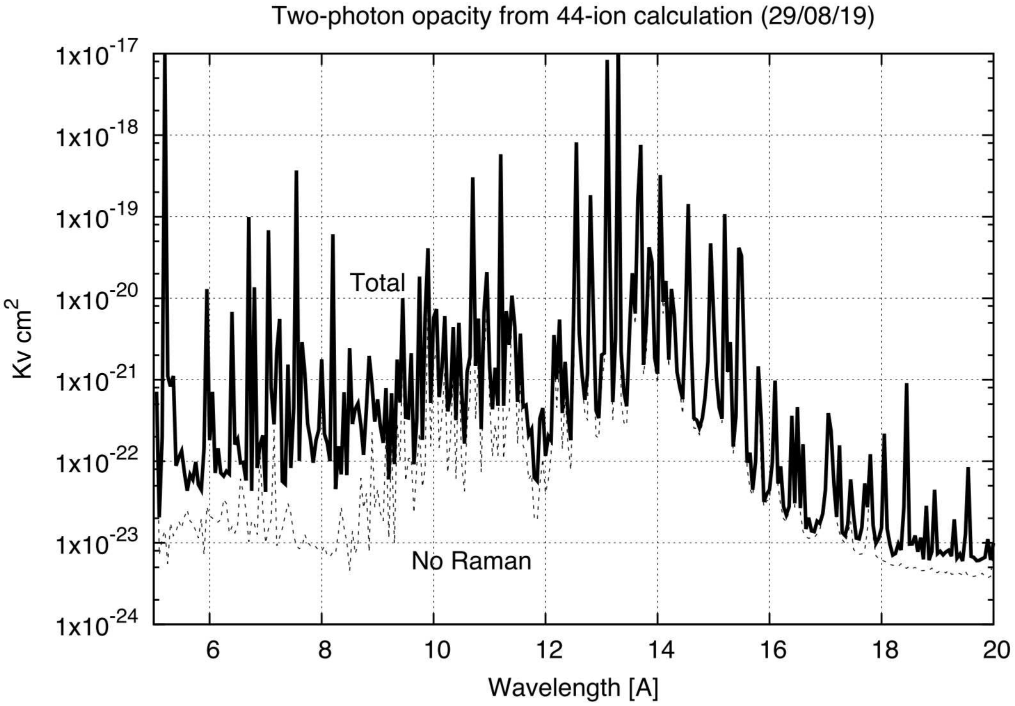

Figure 1: In the 7-10 A range, the Raman effect makes a dominant contribution to the calculated opacity. The frequency average of this absorption cross-section is equivalent to an opacity of about 125 cm2/gram. This is a preliminary result not yet suitable for publication.

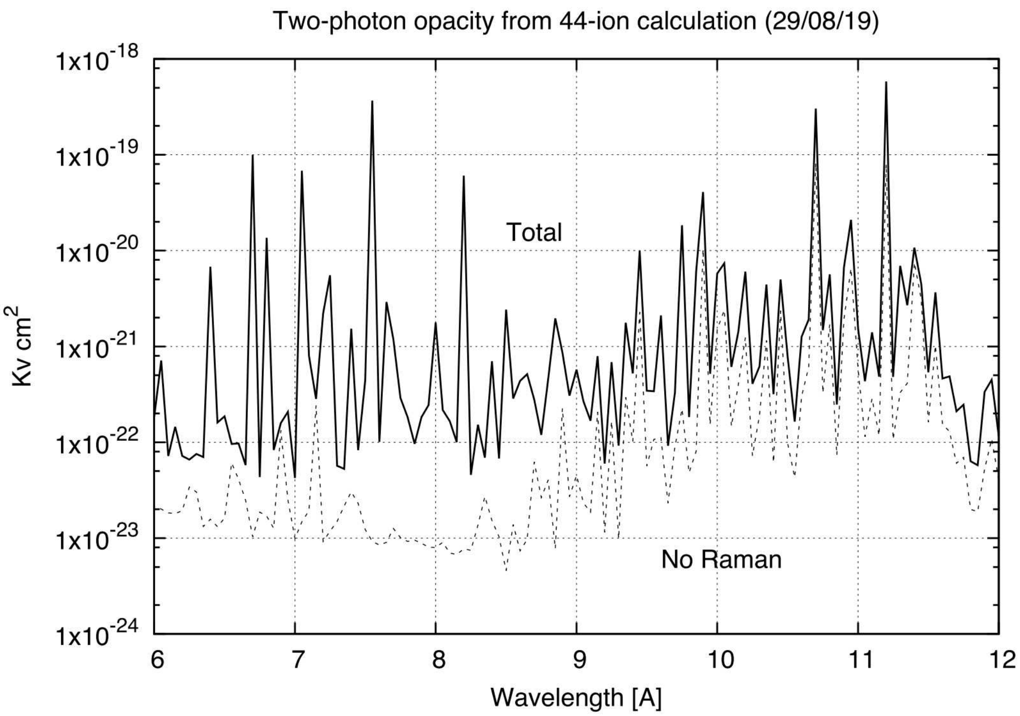

Figure 2 Same data as in Figure 1 plotted on an expanded scale.

IONLIST - 44 ion calculation 26 August, 2019 R. More

ion #	sub name	configuration	ion charge	population
1	ene16	1s2 2s2 2p6	16	0.15018
2	ene17	1s2 2s2 2p5	17	0.15367
3	ene18	1s2 2s2 2p4	18	0.16375
4	ene19	1s2 2s2 2p3	19	0.11375
5	ene15	1s2 2s2 2p6 3s	15	0.00197
6	ene17ex1	1s2 2s1 2p6	17	0.02059
7	ene17ex2	1s2 2s2 2p4 3p	17	0.01360
8	ene14g	1s2 2s2 2p6 3s2	14	0.00545
9	ene14ex	1s2 2s2 2p6 3s3p	14	0.00029
10	fe17e3	1s2 2s2 2p4 3p	17	0.03145
11	fe17e4	1s2 2s2 2p4 3d	17	0.04085
12	fe17e5	1s2 2s1 2p5 3s	17	0.00465
13	fe17e6	1s2 2s1 2p5 3p	17	0.01071
14	fe17e7	1s2 2s1 2p5 3d	17	0.01411
15	fe18e1	1s2 2s2 2p3 3s	18	0.00604
16	fe18e2	1s2 2s2 2p3 3p	18	0.01428
17	fe18e3	1s2 2s2 2p3 3d	18	0.01881
18	fe18e4	1s2 2s1 2p5	18	0.05646
19	fe18e5	1s2 2s0 2p6	18	0.00201
20	fe18e6	1s2 2s1 2p4 3s	18	0.00416
21	fe18e7	1s2 2s1 2p4 3p	18	0.00979
22	fe18e8	1s2 2s1 2p4 3d	18	0.01308
23	fe18e9	1s2 2s0 2p5 3s	18	0.00038
24	fe18e10	1s2 2s0 2p5 3p	18	0.00089
25	fe18e11	1s2 2s0 2p5 3d	18	0.00146
26	fe16e5f	1s2 2s2 2p4 3p 5f	16	0.00183
27	fe16e5d	1s2 2s2 2p4 3p 5d	16	0.00134
28	fe16e4f	1s2 2s2 2p4 3p 5f	16	0.00284
29	fe16ep4f	1s2 2s2 2p5 4f	16	0.01382
30	fe16e4s	1s2 2s2 2p5 4s	16	0.00247

31	fe17e31	1s2 2s2 2p4 4s	17	0.00304
32	fe17e32	1s2 2s2 2p4 4p	17	0.00829
33	fe17e33	1s2 2s2 2p4 4d	17	0.01280
34	fe17e34	1s2 2s2 2p4 4f	17	0.01716
35	fe17e35	1s2 2s1 2p5 4s	17	0.00104
36	fe17e36	1s2 2s1 2p5 4p	17	0.00143
37	fe17e37	1s2 2s1 2p5 4p	17	0.00221
38	fe15e38	1s2 2s2 2p5 3s 4d	15	0.00061

39	fe15e39	1s2 2s2 2p4 3s 3p 4d	15	0.00013
40	fe15e40	1s2 2s2 2p5 3p 4d	15	0.00136

41	fe15e41	1s2 2s2 2p5 3p 4f	15	0.00179
42	fe15e42	1s2 2s2 2p5 3d 4p	15	0.00115
43	fe15e43	1s2 2s2 2p5 3d 4d	15	0.00175
44	fe15e44	1s2 2s2 2p5 3d 4f	15	0.00231

Sum of populations:
sum of 14+ .00574 sum of 15+ .01108
sum of 16+ .17248 sum of 17+ .33562
sum of 18+ .29107 sum of 19+ .11375
Sum of all these = .92973 (about 7.5 % low)

Average opacity < Kv > = 125.94 * 1.075 ~ 135.45 cm2/gram

Ions with large cross-sections on 7 - 10 Angstrom window:
3,10,12,13,15,22,25,28,34,39,40,42,44
Many of these are Raman-Stokes