Outline

- **ATOMIC**
- Electron collisional line broadening
- 3 Models
  - Dimitrijevic & Konjevic modified semi-empirical model (DK)
  - Hey and Breger semi-classical impact parameter model (HB)
  - MERL dedicated line shape code
- Example Application: Basalt
- Detailed Comparison: Ca I, Ca II
- Future Work

Using ATOMIC to model low-temperature plasmas

- **Plasma conditions**
  - \( T_e = 1 \text{eV} \) (13,000K), \( T_i = 0 \)
  - \( N_e \sim 10^8 \text{cm}^{-3} \)
  - \( n_e = 0.2 \)
- **Challenges**
  - The atomic structure of near-neutral systems with large numbers of bound electrons and few free electrons are difficult to solve accurately
  - High resolution spectrometers (1000 to 15,000) exist which are able to resolve very complex spectra (1000s of lines)
- **Simplifications**
  - According to the McWhirter criterion, these systems are usually in LTE for \( N_e \gtrsim 10^7 \text{cm}^{-3} \)
  - \( N_e (\text{cm}^{-3}) \lesssim 1.6 \times 10^{15} \sqrt{T_e (\text{(K)}) \Delta E (\text{eV})}^{0.5} \)
  - Line positions can be supplemented with the NIST database
- **Goals**
  - To achieve accurate Ne values, a better electron collisional line broadening model is required that has previously been used in ATOMIC
  - Collisional electron broadening (TB/CB) is now broadening included, a model which fits the data well will underpredict the Ne values present in the plasma
  - This model must be fast: ATOMIC is required to run multi-element systems with many thousands of lines
- **Can we model 500+ 1000 spectral lines?** Yes

What is Electron collisional line broadening?

- **Stark Broadening**
  - Any species undergoing a transition in a plasma will be subject to collisions from neighboring electrons and ions
- **Semi-classical approximations**
  - Electrons may be treated as particles
  - Electrons follow a classical path
  - Most broadening is caused by weak collisions
  - Strong collisions are rare
  - If not negligible, ion perturbations are quasi-static

D.K. vs. H.B. Models

**D. K. Model**
- Includes both ions and neutrals
- Includes elastic collisions
- No strong collisions
- Gaunt factors:
  - Semi-empirical table based on the Van Regenmortel method, including the Green high temperature limit.
- The velocity average is executed at the most probable velocity (Maxwellian)
- Literature indicates a loss of accuracy for higher ionization stages

**H. B. Model**
- Ion only
- Includes elastic collisions
- Includes strong collisions
- Gaunt factors:
  - Analytic formula based on minimal and maximal impact parameters
  - Incorporates path curvature corrections for higher mass or charge ions
  - Modification to include neutrals is potentially possible
- The velocity average is executed for 0-threshold, and threshold-infinity

**ATOMIC relies on LAN’s atomic kinetics codes**

- CATS (Cowan’s code)
- GIPPER (ionization)
- ATOMIC

<table>
<thead>
<tr>
<th>CATS (Cowan’s code)</th>
<th>GIPPER (ionization)</th>
<th>ATOMIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>RATS (relativistic)</td>
<td>LTE or NLTE Multi-element plasmas</td>
<td></td>
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</tbody>
</table>

fine structure or configuration averaged
- UTAs and MUTAs
- e\(^-\) ionization photoionization autoionization
- energy levels
- Supplement CATS with NIST tables of g\(^f\) values
- \( e\(^-\) \) excitation

**Why do we think ATOMIC needs better line broadening?**

- **ATOMIC’s hydrogenic model overestimates electron collisional broadening**
- **Distant continuum states are overestimated.**
- **The ATOMIC hydrogenic model does not include a gaunt factor, which would scale transitions relative to E/\( \Delta E \), and reduce broadening.**
- **Experiment:** L44N high resolution LIB - 10,000 resolving power, 6-nm laser
- **Model Emulsion:** \( T_e = 0.8 \text{eV}, N_e = 1.0 \times 10^7 \text{cm}^{-3}, Q> = 0.95 \)

**ATOMIC’s new line broadening model**

**Modifications**
- In the literature, hydrogenic cross section information has been used for semi-classical models.
- ATOMIC will use configuration averaged oscillator strengths calculated by CATS
- Elastic / Inelastic Threshold
  - Below E/\( \Delta E \) = 1, (threshold), broadening is from elastic collisions, with gaunt factor \( \approx 0.2 \)
  - This results in a simplified thermal average in both models.
- Strong Collisions
  - Strong collisions violate the semi-classical model constraint \( E < I \), but can contribute up to an additional 30% broadening.

**Two semi-classical models to test and compare:**

\[
W = \frac{a_{ei}^2 N_e}{8 \pi \hbar c} \int \frac{d \omega}{\omega} \sum \left( \frac{\hbar c}{\omega} \right) \sum \left( \frac{\hbar c}{\omega} \right) \frac{m_i R_i}{m_e R_e} \left( \frac{m_i}{m_e} \right)^{1/2} \frac{1}{\beta_{ei}} \frac{1}{\beta_{ei}}
\]

\[
W = \frac{a_{ei}^2 N_e}{8 \pi \hbar c} \int \frac{d \omega}{\omega} \sum \left( \frac{\hbar c}{\omega} \right) \sum \left( \frac{\hbar c}{\omega} \right) \frac{m_i R_i}{m_e R_e} \left( \frac{m_i}{m_e} \right)^{1/2} \frac{1}{\beta_{ei}} \frac{1}{\beta_{ei}}
\]

**D. K.**

**H. B.**
Ca II 4s-4p doublet: Model Comparison

- Two ATOMIC calculations for the Ca II 4s-4p doublet at 393nm and 397nm.
- Running ATOMIC at the conditions of experimental Stark width measurements allows comparison of the theoretical and experimental widths for the old(red) and new(black) lineshapes models.
  - $\Delta \nu = 1.05eV, \text{Ne} = 0.8\times10^{13} \text{cm}^{-3}$
  - $\Delta \nu = 1.73eV, \text{Ne} = 1.3\times10^{13} \text{cm}^{-3}$

Real Application: Basalt

- LIBS = laser induced breakdown spectroscopy
- Applications for geochemistry, archaeology, and industry.
- Curiosity Rover: ChemCam
  - Rapid, remote rock identification
  - Search for hydration and organic compounds
- Basalt (BIR1)
  - Complex multi-element system: Si, Ti, Al, Mg, Ca, Na, K, P, O, F, Mn
  - Also requires H, O, and C to account for sample hydration and a CO$_2$ atmosphere
- ChemCam standards have established composition.  

Future Work: Comparison with MERL

- MERL is a dedicated, stand-alone model for isolated lines, which represents a useful comparison for ATOMIC’s new line broadening model.
- Pros
  - Like ATOMIC, this includes Doppler broadening
  - Includes plasma electric microfield$^2$
  - Gaunt factors are determined via partial wave sums based on the work of Karzas & Lattner$^3$
  - Includes a more detailed lineshape model than ATOMIC
- Cons
  - Does not include strong collisions or elastic collisions.
  - Evaluating atomic kinetics data with a pre-CATs version of Cowan’s code requires a substantial time commitment.
  - Will run well only if the plasma conditions and atomic kinetics are narrowly focused on the line in question.
  - Utilizing MERL for near-neutrals is computationally expensive.
- Running both MERL and ATOMIC in regimes where the two models have consistent physics grants the opportunity to evaluate how much utilizing configuration averaged oscillator strengths can change the line broadening.

Ca I and Ca II, vs. Experiment

- Many experiments attempting to measure Stark widths for various ions and neutrals exist in the literature, but not all are of equal quality.
- Several publications like 3 compare these experiments and their relative quality BUT IT is still necessary to have a good understanding of each experiment before attempting to model it.
  - $^{1}$D.K. = Dimitrijevic & Konjevic inspired model
  - $^{2}$H = ATOMIC’s original hydrogenic model

<table>
<thead>
<tr>
<th>Ref</th>
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<th>$\Delta \nu$ (10$^{13}$cm$^{-3}$)</th>
<th>$\nu_{max}$</th>
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<th>$\nu_{max}$</th>
<th>D.K. $%$ difference</th>
<th>H. $%$ difference</th>
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Before and After: D.K. Model

- Our model of Basalt involves radiation transport through three plasma layers, however, in this spectral region, the Basalt spectrum is optically thin.
- $\Delta \nu = 3eV, 0.9eV, 0.6eV$
- $p = 5e-6$g/cm$^3$, $e-6$g/cm$^3$, $e-7$g/cm$^3$ ($p$ = per ion fraction)

We have used P. Hakeil’s radiation transport model FEST$^2$

Summary and Future Work

- To accurately model low-temperature plasmas with high resolution, the treatment of electronic collision line broadening in ATOMIC needed improvement.
- Using a modernized version of the Dimitrijevic and Konjevic line broadening model, ATOMIC can successfully treat plasmas with spectral resolving power $\sim 1000$.
- Modeling 11,500-15,000 resolving power is a continuing goal.
- Future work for an upcoming publication:
  - Utilize the modernized Hey and Breger model to evaluate the importance of strong collisions, gaufter factors with improved physics, and an improved treatment of the path curvature of electrons for higher charged ions.
  - Use MERL to evaluate the potential loss of accuracy due to utilizing the impact parameter approximation and configuration averaged oscillator strengths for line broadening.
- Compare with measured Stark widths for additional elements.