A two-step model for studying ionization potential depression in dense plasmas

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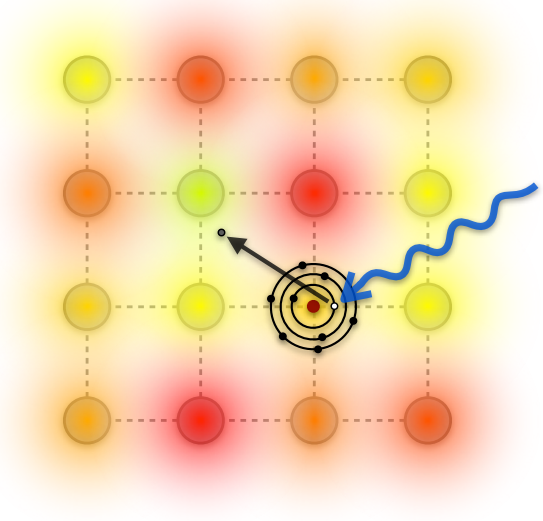
Average Atom Models for Warm Dense Matter
Berkeley, United States (online) / June 28–29, 2021



HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

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Center for Free-Electron Laser Science
CFEL is a scientific cooperation of the three organizations:
DESY – Max Planck Society – University of Hamburg

DESY.

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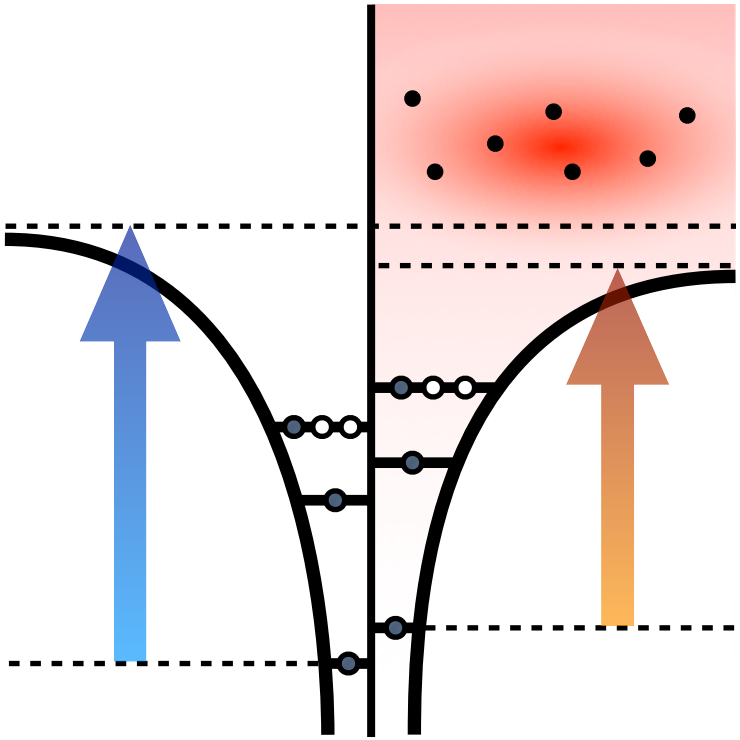
DESY.

Ionization Potential Depression (IPD)

isolated atom

- Coulomb potential by the nucleus
- screening by bound electrons



solid / plasma

Dense environment

+ screening by free electrons

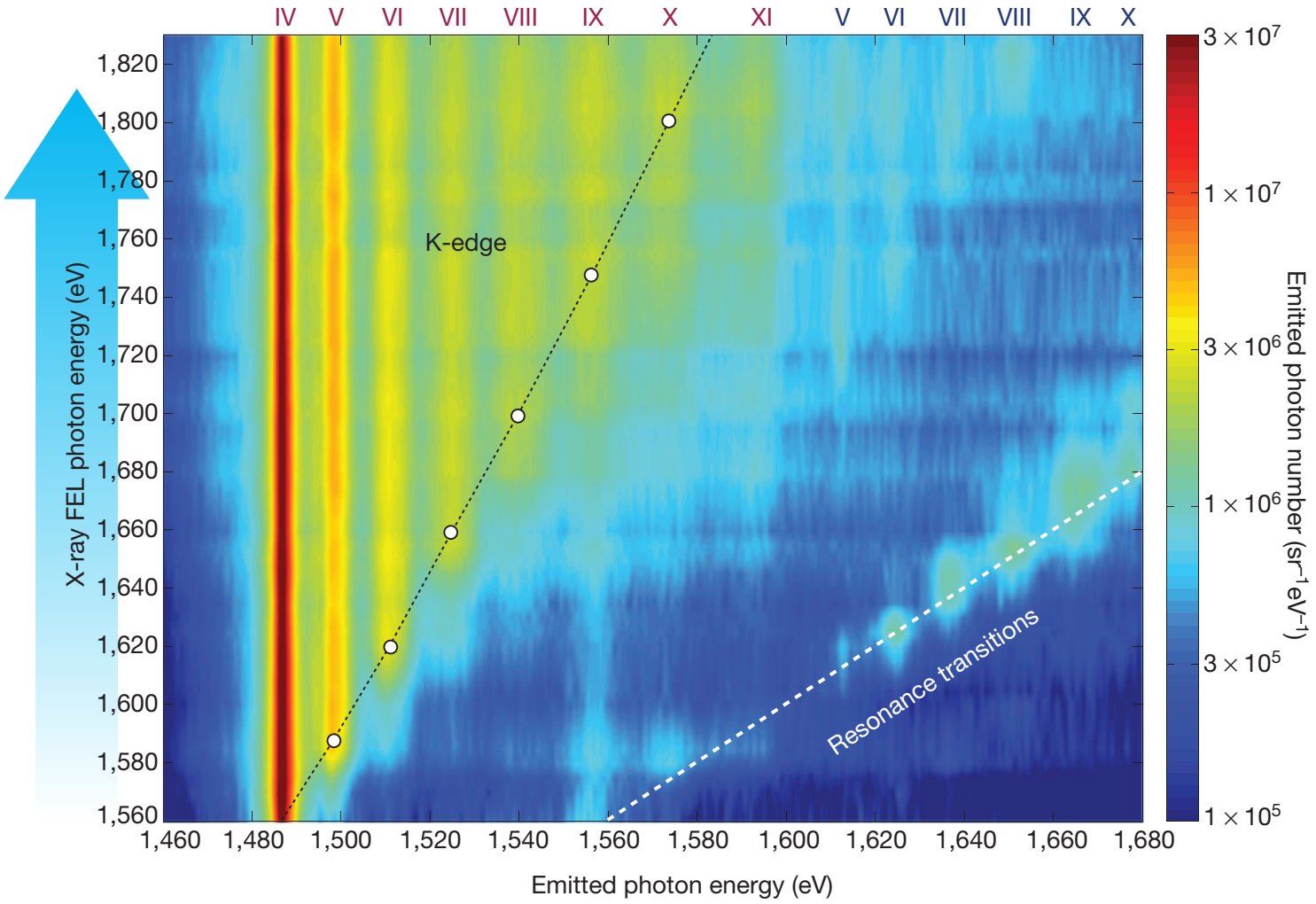
+ pressure ionization

➔ IP lowering

One of the most fundamental physics for atomic processes in a dense plasma

IPD: $\Delta E_i = \mathrm{IP}_i^{\mathrm{iso}} - \mathrm{IP}_i^{\mathrm{pla}}$

Warm dense Al plasma (XFEL experiment)



$T < 200$ eV
solid density
(2.7 g/cm^3)

Vinko *et al.*, *Nature* **482**, 59 (2012);

Ciricosta *et al.*, *Phys. Rev. Lett.* **109**, 065002 (2012).

Two-step model: overview

- Two-step model based on
  - Quantum-mechanical calculation: Hartree-Fock-Slater method
  - muffin-tin approximation
  - pseudocontinuum calculation

First step

Average-atom calculation

Second step

fixed-configuration calculation

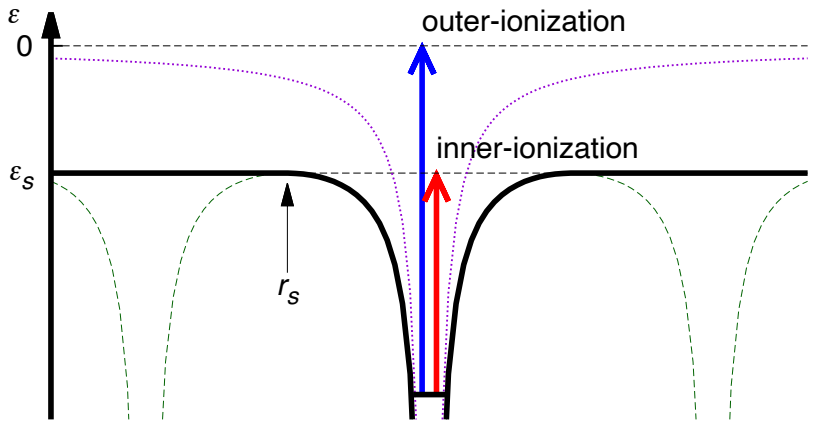
Son, Thiele, Jurek, Ziaja & Santra, *Phys. Rev. X* **4**, 031004 (2014).

Hartree-Fock-Slater / muffin-tin potential

- Solve the Schrödinger equation (SE)

$$\hat{H} = -\frac{1}{2}\nabla^2 + V(\mathbf{r})$$

$$\hat{H}\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$



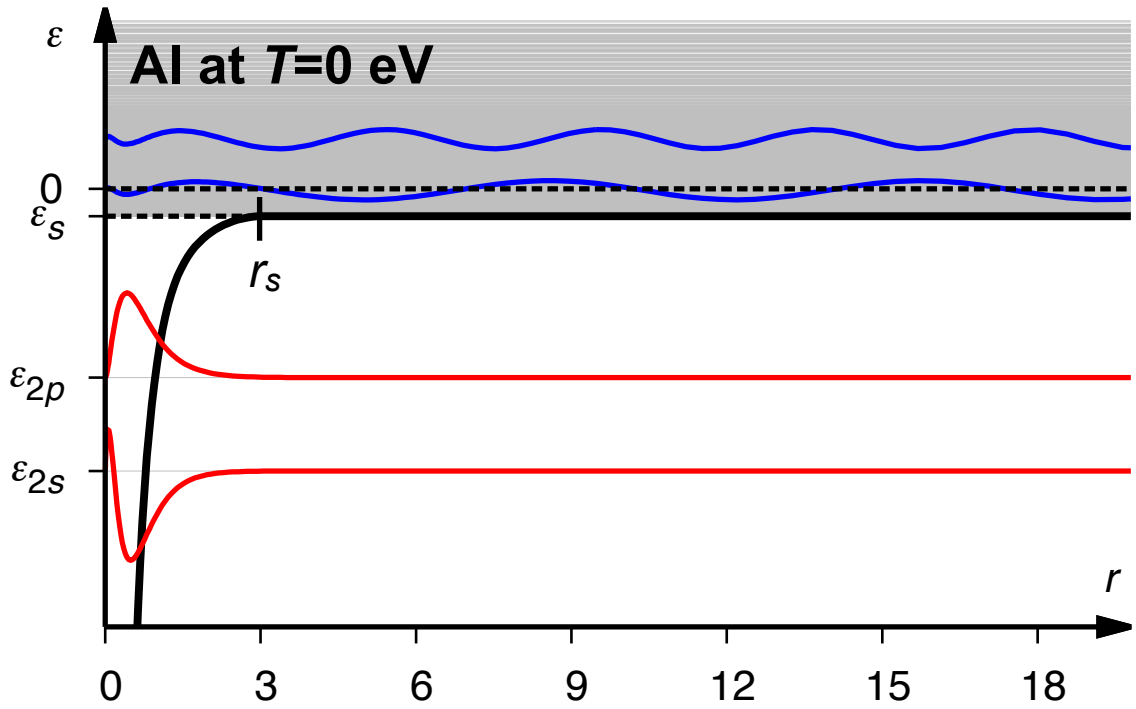
- HFS potential inside the WS radius / muffin-tin flat potential outside

$$V(\mathbf{r}) = \begin{cases} -\dfrac{Z}{r} + \displaystyle\int_{r' \le r_s} d^3r' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\mathrm{x}}[\rho(\mathbf{r})] & \text{for } r \le r_s \\ V(r_s) \ (= \varepsilon_s) & \text{for } r > r_s \end{cases}$$

- Slater exchange potential: $V_{\mathrm{x}}[\rho(\mathbf{r})] = -\frac{3}{2}\left[\frac{3}{\pi}\rho(\mathbf{r})\right]^{1/3}$

- Spherical averaging: $\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r)\right] u_{nl}(r) = \varepsilon_{nl} u_{nl}(r)$

Continuum-state calculation



- $\varepsilon \geq \varepsilon_s$: pseudocontinuum
- $\varepsilon < \varepsilon_s$: bound

r_s ~ 3 a.u.

r_{max}=100 a.u. in calculation

- non-uniform radial grid: N_r=200, $0 \leq l \leq 30$ ➔ 6200 (n,l)-eigenstates
- no boundary condition at all at r_s
- no distinction b/w bound and continuum states
- pseudocontinuum approach: widely used in strong-field atomic physics

cf) Gérard Massacrier's talk and *PRR* **3**, 023026 (2021).

Finite-temperature calculation

- Grand-canonical ensemble at a finite temperature T
- Solve SE with $\hat{H} = -\frac{1}{2}\nabla^2 + V\left[\rho(\mathbf{r}, T)\right]$
- Electronic density (bound & continuum) $\rho(\mathbf{r}, T) = \sum_p \left|\psi_p(\mathbf{r})\right|^2 \bar{n}_p(\mu, T)$
- Fermi-Dirac distribution $\bar{n}_p(\mu, T) = \frac{1}{e^{(\varepsilon_p - \mu)/T} + 1}$
- Chemical potential $Z - \sum_p \left(\int_{r \le r_s} d^3r \ \left|\psi_p(\mathbf{r})\right|^2 \right) \bar{n}_p(\mu, T) = 0$
- Assumption: thermalized hot electrons; cold ions
- Input parameters: element (Z), temperature (T), and ion density (via r_s)

This AA model has been implemented within **XATOM**

Son *et al.*, *Phys. Rev. A* **83**, 033402 (2011); Jurek *et al.*, *J. Appl. Cryst.* **49**, 1048 (2016);
http://www.desy.de/~xraypac

Benchmark calculations of XATOM-AA

- For Al at T=0 eV, avg. Q is +3 and Fermi E is 8.0 eV (EXP: 11.7 eV).
- For Fe at T=0 eV, avg. Q is +8 and Fermi E is 7.9 eV (EXP: 11.1 eV).
- For Al at low temperatures,

	T=10 eV, solid density		T=5 eV, 0.1×solid density		
Level	Present	Sahoo(2008)	Present (HFS)	Present (LDA)	Johnson(2006)
1*s*	–1530.1	–1495.0	–1547.3	–1501.8	–1501.8
2*s*	–102.5	–101.2	–119.6	–108.2	–108.3
2*p*	–64.9	–63.9	–82.0	–70.9	–71.0
3*s*		–6.3	–8.6	–7.0	–7.0
3*p*			–2.5	–1.4	–1.5
μ	–1.5		–11.1	–10.3	–10.4
avg. Q	+3.01	+2.38	+1.34	+1.45	+1.49

Sahoo *et al.*, *Phys. Rev. E* **77**, 046402 (2008); Johnson *et al.*, *JQSRT* **99**, 327 (2006).

Average-atom results for Al plasma

- Self-consistently determined: orbitals, orbital energies, electron density, muffin-tin flat potential ε_s, and chemical potential μ

Al
solid density
Z=13
n_i=2.7 g/cm^3

T	$\bar{Q}$	ε_{1s}	$\cdots$	ε_s	μ
10	+3.01	−1541.14		−11.03	−12.57
30	+3.95	−1579.28		−12.46	−58.67
40	+4.83	−1606.37		−13.19	−85.66
60	+5.67	−1657.70		−14.33	−145.43
80	+6.87	−1702.23		−15.15	−211.69

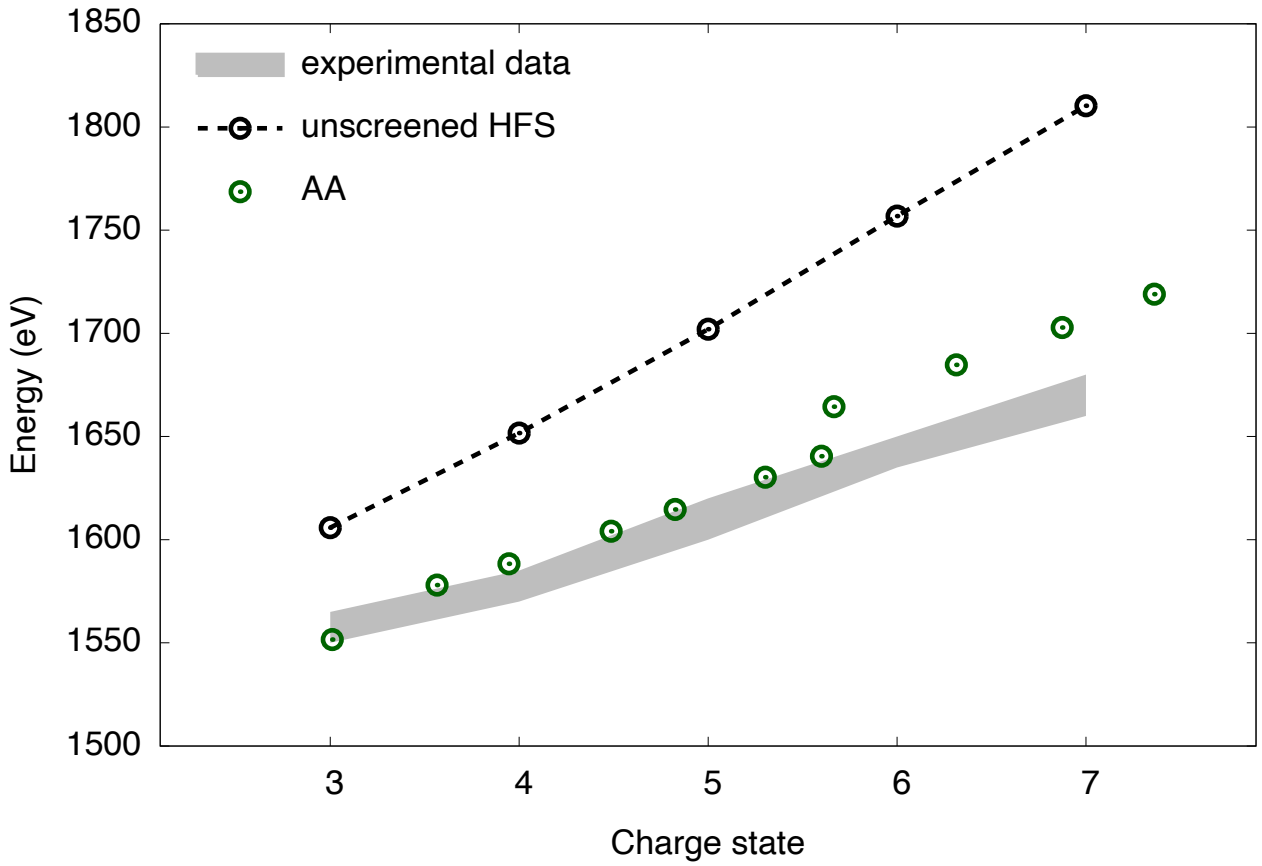
ensemble-averaged charge and orbital energies

Ionization potential calculation:

$$\mathrm{IP} = \begin{cases} \varepsilon_s - \varepsilon_{1s} & (\mu \leq \varepsilon_s) \\ \mu - \varepsilon_{1s} & (\mu > \varepsilon_s) \end{cases}$$

cf) Suxing Hu's talk and *PRL* **119**, 065001 (2017).

Ionization potential with AA only



Problem with ensemble-averaged charges? No such things in experiment!

AA as first step: more than average

Al at T=80 eV

Q	Configuration	Probability	E_K	$E_{K\alpha}$
+5	$1s^2 2s^1 2p^4 3s^0 3p^1$	0.0193	1618.3	1497.7
	$1s^2 2s^2 2p^3 3s^0 3p^1$	0.0187	1623.1	1500.3
	$1s^2 2s^2 2p^4 3s^0 3p^0$	0.0174	1578.7	1486.7
+6	$1s^2 2s^1 2p^3 3s^0 3p^1$	0.0376	1658.1	1511.6
	$1s^2 2s^1 2p^4 3s^0 3p^0$	0.0349	1618.3	1497.7
	$1s^2 2s^2 2p^3 3s^0 3p^0$	0.0339	1623.1	1500.3
	$1s^2 2s^2 2p^2 3s^0 3p^1$	0.0205	1663.5	1514.5
	$1s^2 2s^1 2p^3 3s^1 3p^0$	0.0139	1656.0	1511.3
+7	$1s^2 2s^1 2p^3 3s^0 3p^0$	0.0681	1666.3	1512.8
	$1s^2 2s^1 2p^2 3s^0 3p^1$	0.0413	1705.4	1527.8
	$1s^2 2s^2 2p^2 3s^0 3p^0$	0.0371	1671.9	1515.8
	$1s^2 2s^0 2p^3 3s^0 3p^1$	0.0189	1699.3	1524.5
	$1s^2 2s^0 2p^4 3s^0 3p^0$	0.0175	1660.9	1509.9
	$1s^2 2s^1 2p^2 3s^1 3p^0$	0.0153	1705.4	1527.9
	$1s^2 2s^2 2p^1 3s^0 3p^1$	0.0120	1711.7	1531.2
+8	$1s^2 2s^1 2p^2 3s^0 3p^0$	0.0747	1718.7	1530.0
	$1s^2 2s^0 2p^3 3s^0 3p^0$	0.0342	1712.3	1526.7
	$1s^2 2s^1 2p^1 3s^0 3p^1$	0.0241	1758.5	1546.5
	$1s^2 2s^2 2p^1 3s^0 3p^0$	0.0217	1725.1	1533.4
	$1s^2 2s^0 2p^2 3s^0 3p^1$	0.0207	1751.6	1542.9
+9	$1s^2 2s^1 2p^1 3s^0 3p^0$	0.0437	1775.1	1549.6
	$1s^2 2s^0 2p^2 3s^0 3p^0$	0.0375	1768.0	1545.9
	$1s^2 2s^0 2p^1 3s^0 3p^1$	0.0121	1808.2	1564.1
+10	$1s^2 2s^0 2p^1 3s^0 3p^0$	0.0219	1827.4	1568.1
	$1s^2 2s^1 2p^0 3s^0 3p^0$	0.0106	1835.2	1572.1

$$1s^{n_1}\ 2s^{n_2}\ 2p^{n_3}\ 3s^{n_4}\ 3p^{n_5}\ 3d^{n_6}\ 4s^{n_7}\ 4p^{n_8}\ \cdots$$

bound: n_b | continuum: $n_{p'}$

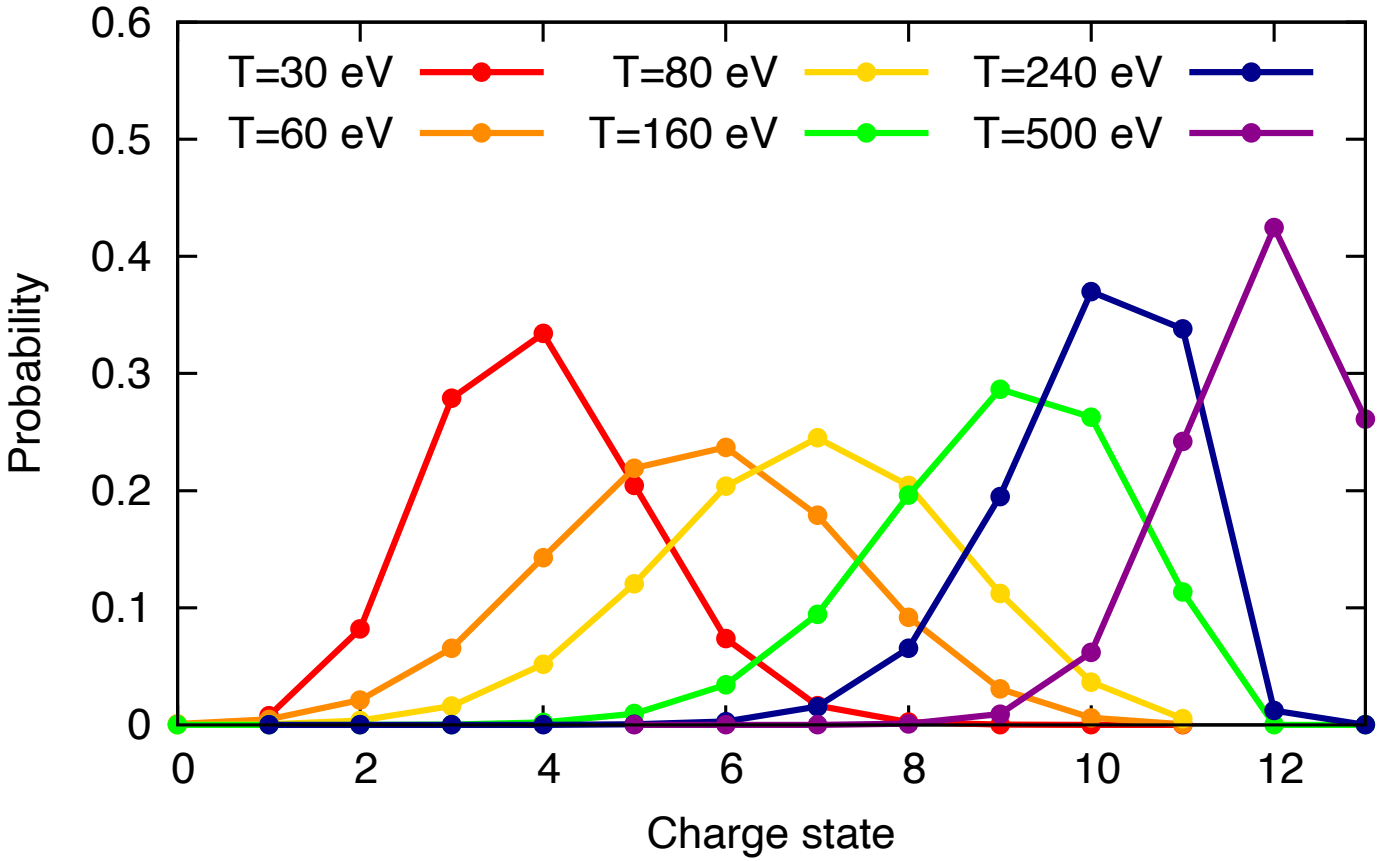
From the grand-canonical ensemble, probability distributions calculated for given bound-state configurations

$$P_{[n_b]} = \sum_{\{n_p\}=\{n_b;n_{p'}\}} P_{\{n_p\}}$$

$$= \prod_{b}^{\text{bound}} \frac{e^{-(\varepsilon_b-\mu)n_b/T}}{1+e^{-(\varepsilon_b-\mu)/T}}$$

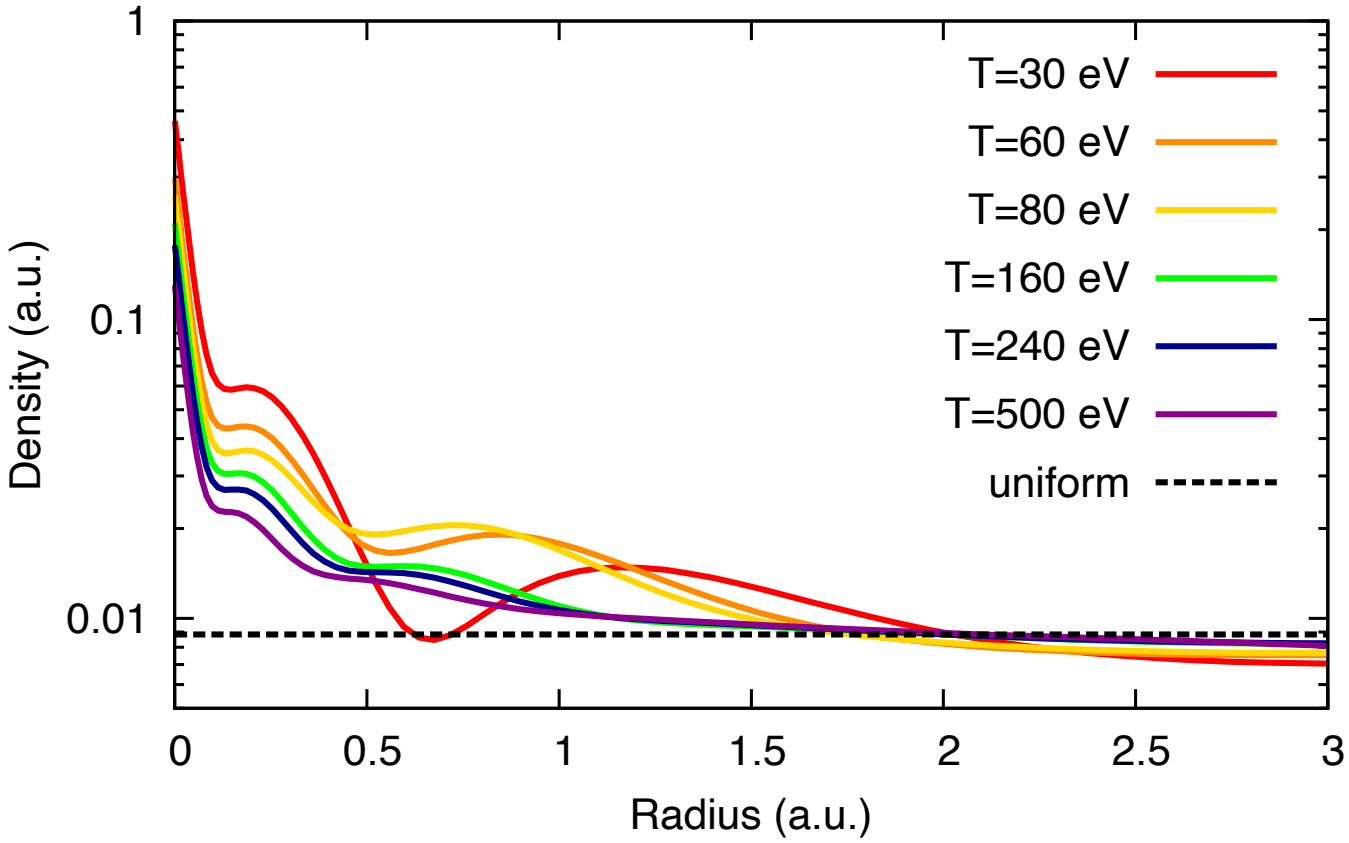
Pei & Chang, *JQSRT* **64**, 15 (2000).

AA as first step: charge-state distribution



$$P_{[n_b]} = \prod_{b}^{\text{bound}} \frac{e^{-(\varepsilon_b - \mu) n_b / T}}{1 + e^{-(\varepsilon_b - \mu)/T}} \Rightarrow P_Q = \sum_{[n_b]}^{Q} P_{[n_b]}$$

AA as first step: free-electron density



After averaging all possible free-electron configurations

$$\rho_f(\mathbf{r}, T) = \sum_{p}^{\text{continuum}} |\psi_p(\mathbf{r})|^2 \, \bar{n}_p(\mu, T)$$

Second step: fixed-config. calculation

- Connection between first step and second step
  - picking up one bound-electron configuration: most probable one
  - constructing a free-electron density
- Performing a new SCF calculation with the fixed free-electron density

$$\hat{H} = -\frac{1}{2}\nabla^2 + V\left[\rho(\mathbf{r};T)\right]$$

$$\rho(\mathbf{r};T) = \sum_{b}^{\text{bound}} \left|\psi_b(\mathbf{r})\right|^2 n_b + \sum_{p}^{\text{continuum}} \left|\psi_p(\mathbf{r})\right|^2 \bar{n}_p(\mu,T)$$

self-consistently updated

fixed

2nd step: *K*-shell ionization & transition *E*

Al at *T*=80 eV

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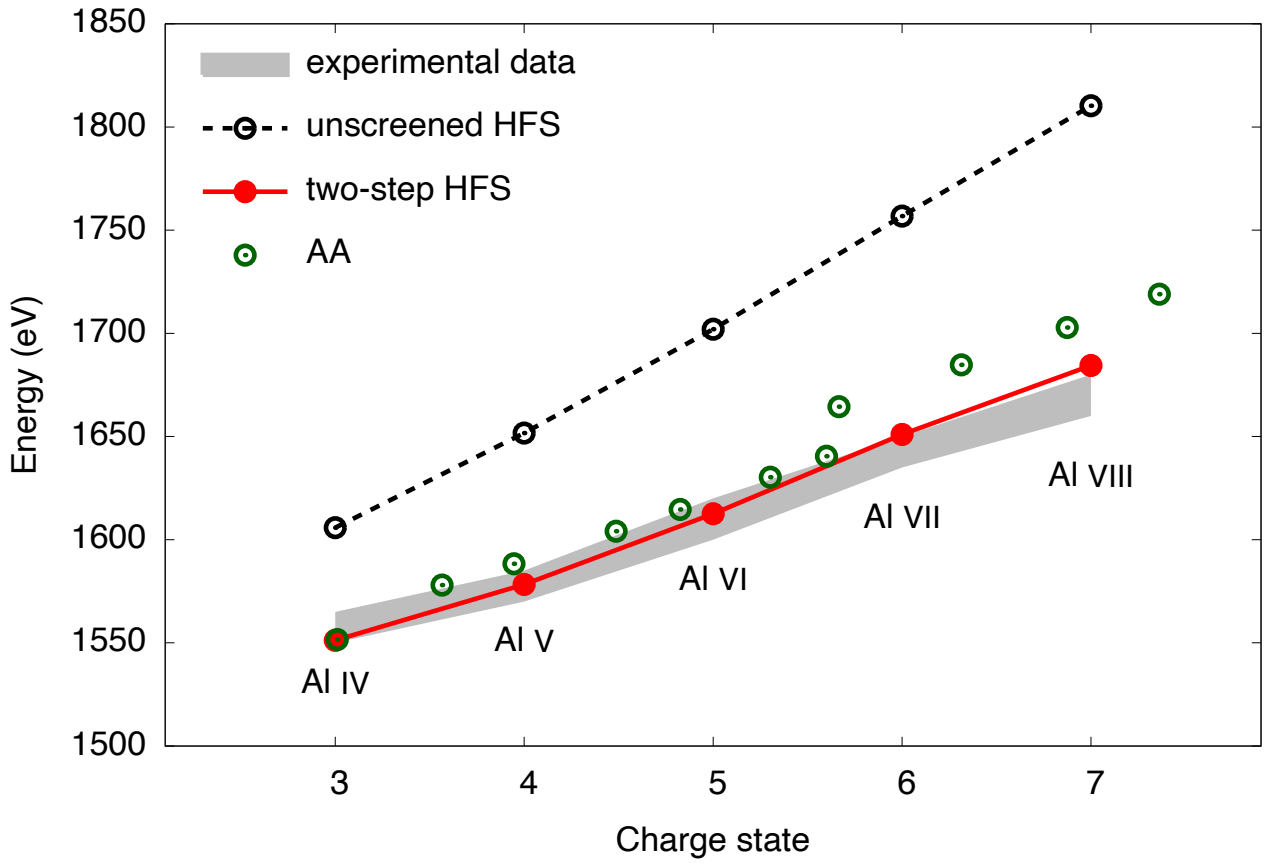
	$1s^2 2s^1 2p^0 3s^0 3p^0$	0.0106	1835.2	1572.1

- SCF calculation for each config.
- individual configurations: different IPs and *K*α lines
- ground-state configuration ≠ the most probable configuration
- *M*-shell electrons do not alter the *K*α lines that much
  ➔ K^nL^m labeling makes sense

cf) Iglesias, *HEDP* **12**, 5 (2014).

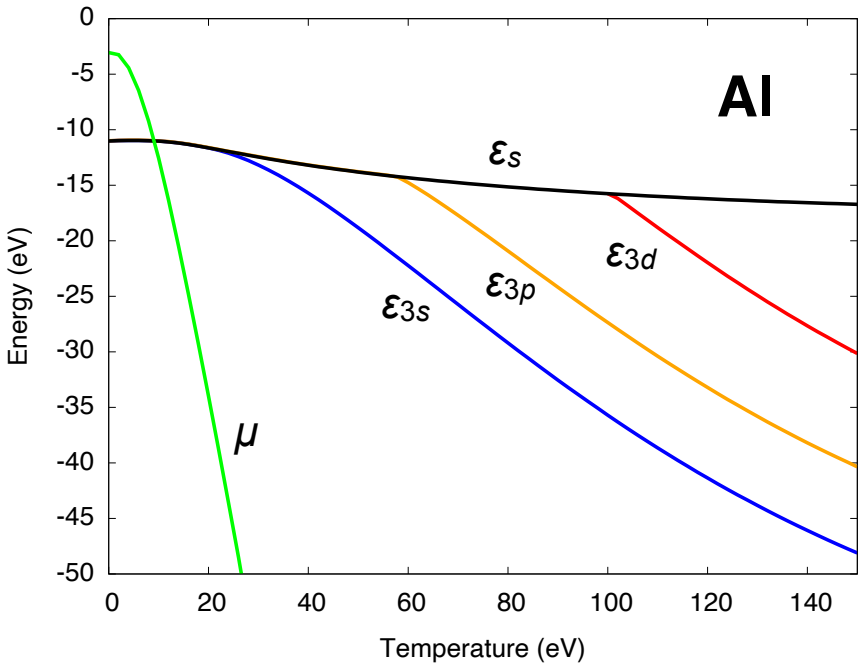
T	$\bar{Q}$	Q_{mp}	C_{mp}
10	+3.01	+3	$1s^2 2s^2 2p^6$
30	+3.95	+4	$1s^2 2s^2 2p^5$
40	+4.83	+5	$1s^2 2s^2 2p^4$
60	+5.67	+6	$1s^2 2s^2 2p^3$
80	+6.87	+7	$1s^2 2s^1 2p^3$

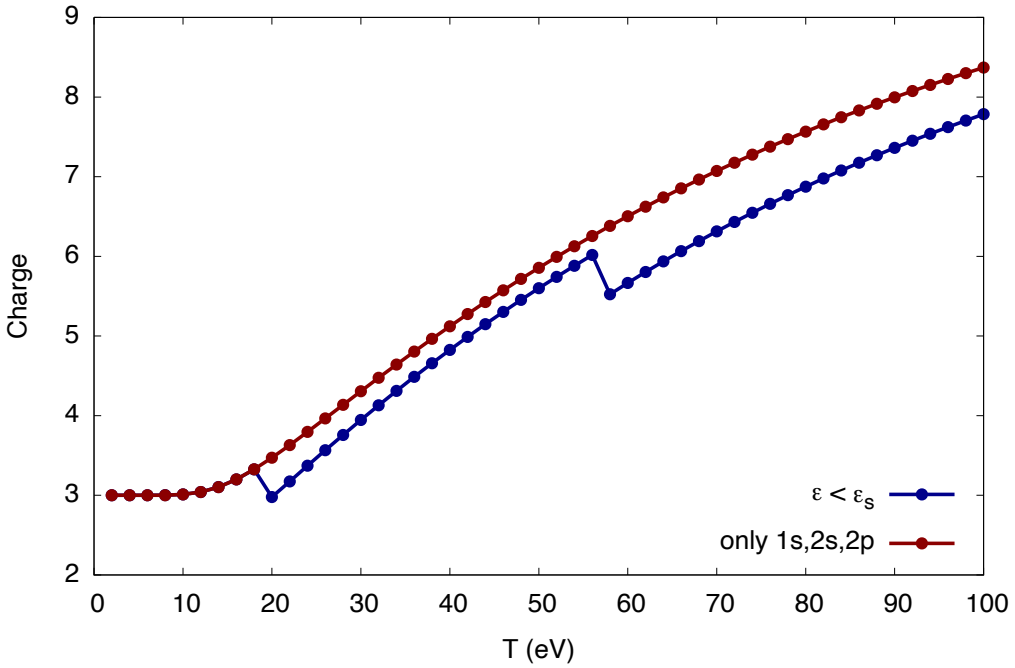
Ionization potential with two-step model



Son, Thiele, Jurek, Ziaja & Santra, *Phys. Rev. X* **4**, 031004 (2014).

How to define atomic charges in AA





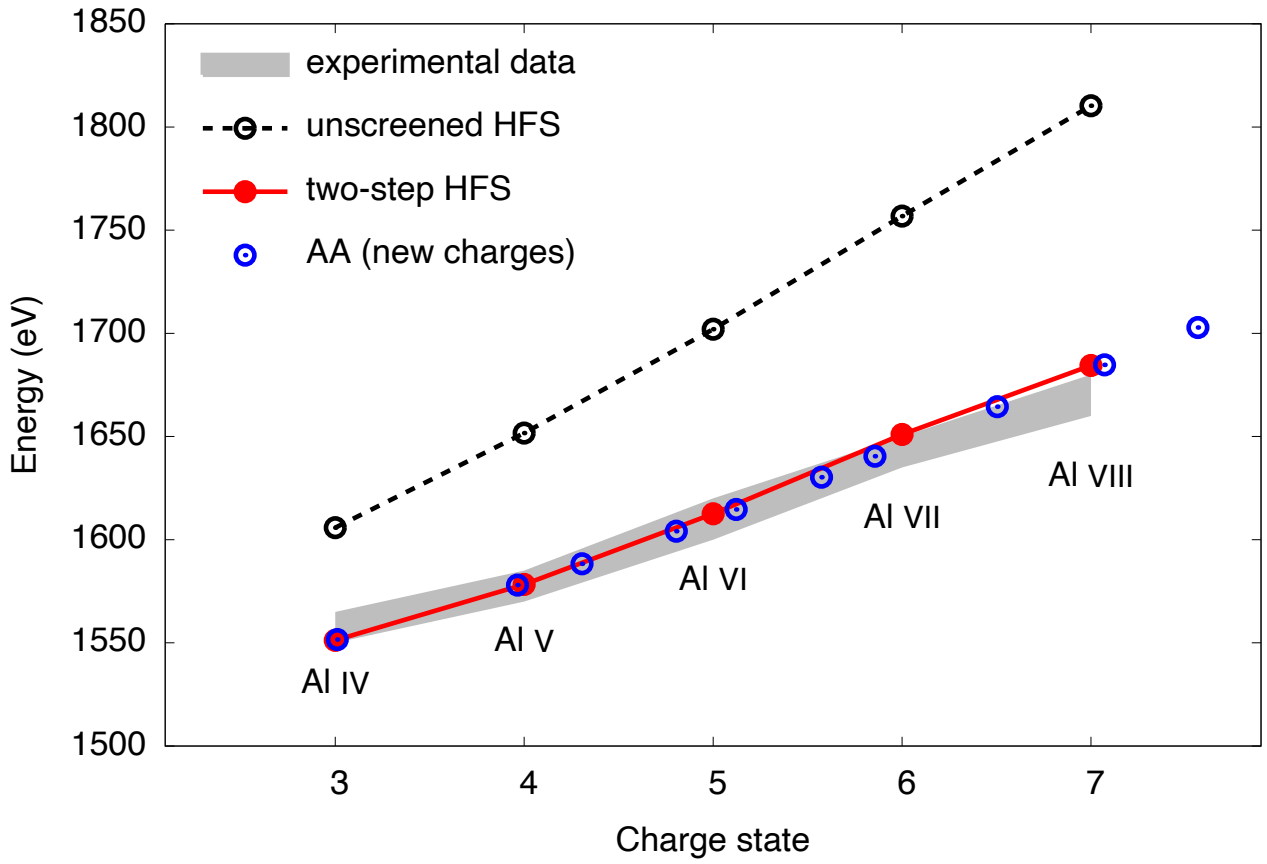
- $\varepsilon < \varepsilon_s$: bound
- $\varepsilon \geq \varepsilon_s$: (pseudo)continuum

Bekx *et al.*, *Phys. Rev. Res.* **2**, 033061 (2020).

Based on bound electron: $\bar{Q} = Z - \sum_{p}^{\varepsilon_p<\varepsilon_s} \frac{(4l_p+2)}{e^{\beta(\varepsilon_p-\mu)}+1}$

K^nL^m labelling: $\bar{Q}' = Z - \sum_{p=1s,2s,2p} \frac{(4l_p+2)}{e^{\beta(\varepsilon_p-\mu)}+1}$

Ionization potential with AA (new charges)

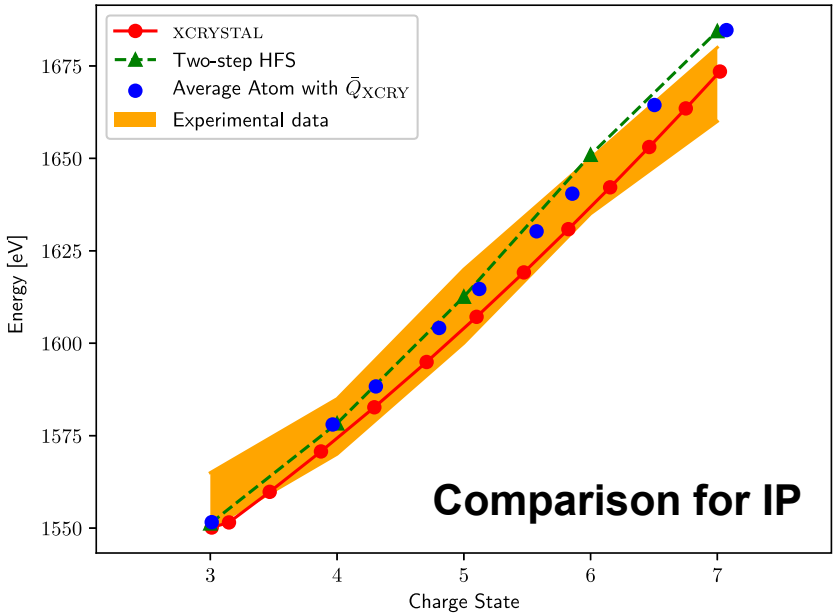


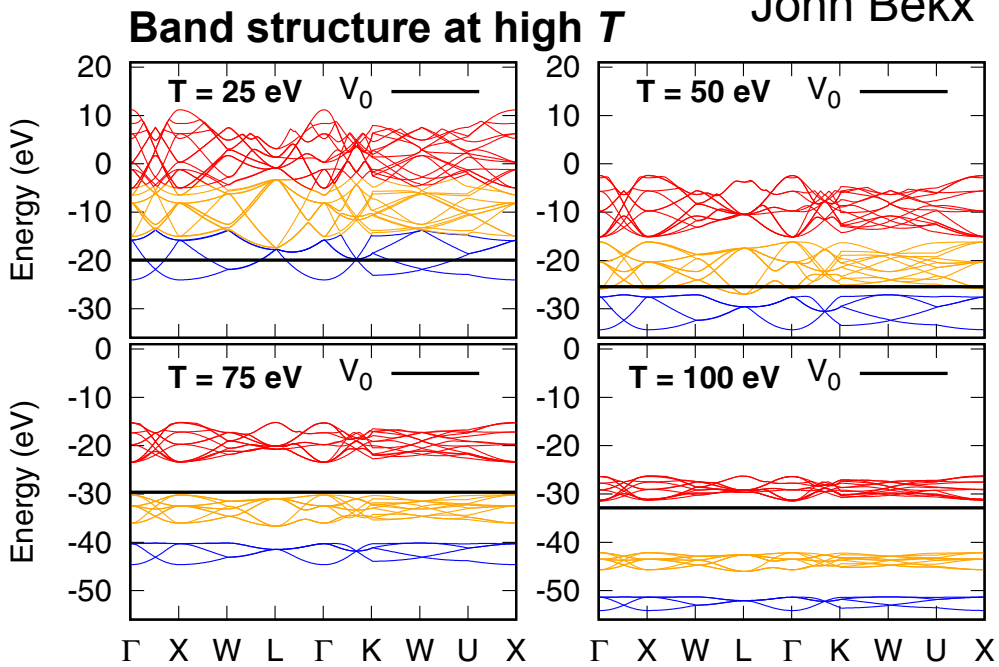
AA is applicable to predict IP values for different atomic charges

Beyond atomic picture: XCRYSTAL

- **XCRYSTAL**: finite-temperature HFS with the Bloch-wave approach within a periodic atomic lattice
- hybrid basis: localized core orbitals + plane wave
- no pseudopotential required

John Bekx





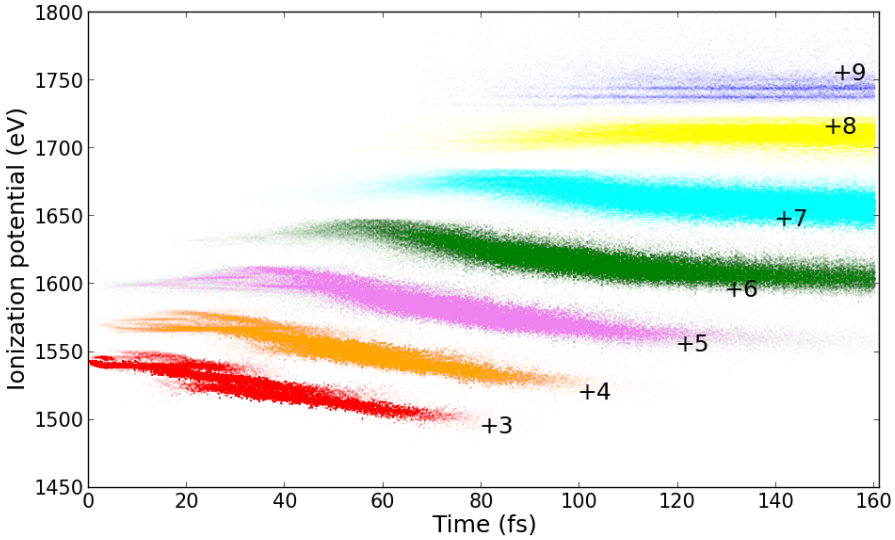
Bekx *et al.*, *Phys. Rev. Res.* **2**, 033061 (2020).

Beyond average picture: XMDYN + XPOT

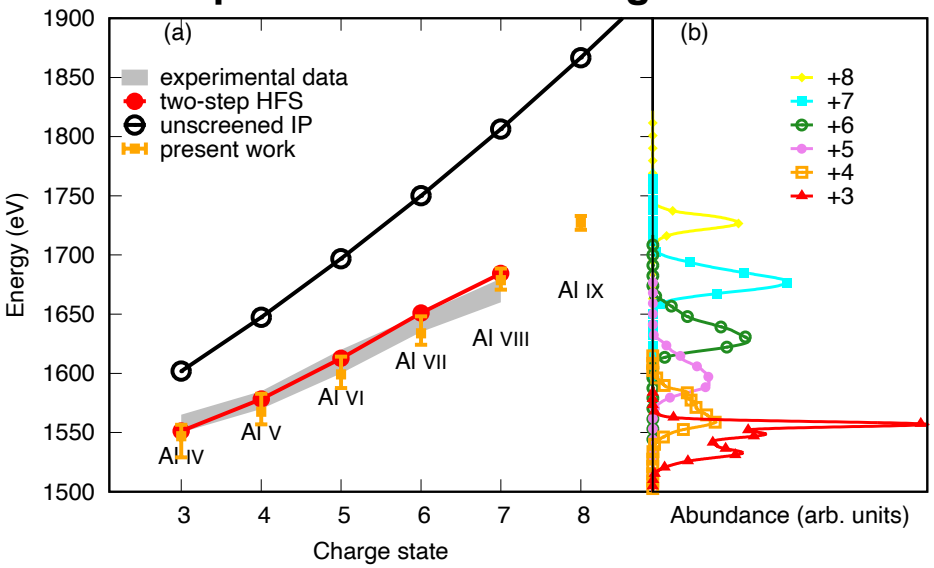
- **XMDYN**: quantum for bound electrons, classical for free electrons and ions ➔ Monte-Carlo Molecular Dynamics (MCMD)
- **XPOT**: enables quantum calculation with a plasma environment at any given time *t* ➔ NLTE approach for IPD

Rui Jin

Time-resolved IP:
Al interacting with 80-fs XFEL pulse



Comparison for time-integrated IP



Jin *et al.*, *Phys. Rev. E* **103**, 023203 (2021).

Conclusion

- Two-step model: first-principles calculation combining average-atom model and fixed-configuration model
- Accurately and efficiently describes atomic properties within plasmas
- Focused on IPD effects of Al plasmas: good agreement with XFEL exp.
- New implementation for AA model within XATOM: simple and robust
- AA model: good description for IP & population analysis (e.g. CSD)
- Beyond AA model: finite-temperature crystalline calculation and non-thermal equilibrium simulation for studying transient IPD

Thank you for your attention!