Quantum-state-resolved ionization dynamics induced by x-ray free-electron laser pulses

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Abstract

Intense **x-ray free-electron laser (XFEL)** pulses can induce multiple sequences of inner-shell ionization events and accompanying decay processes in atoms, producing highly-charged atomic ions. In general, x-ray multiphoton ionization dynamics have been described in terms of time-dependent populations of the electronic configurations visited during the ionization dynamics, neglecting individual state-to-state transition rates and energies. Combining a state-resolved electronic-structure method based on first-order many-body perturbation theory [1] with a Monte Carlo rate-equation method [2] enables us to study state-resolved dynamics based on time-dependent quantum-state populations. Here we present a theoretical study of **state-resolved x-ray multiphoton ionization dynamics** of atoms. Our results demonstrate that configuration-based and state-resolved calculations provide similar charge-state distributions, but differences are visible when resonant excitations are involved. Calculated **time-resolved spectra of electrons and photons** allow us to investigate ultrafast dynamics of x-ray multiphoton ionization in detail. In addition, we will present a comparison with a recent experiment on Ne [3], a theoretical study of electron-cloud alignment dynamics of Ar induced by an XFEL pulse [4], and a discussion of how to handle the extremely large number of atomic parameters involved in state-resolved dynamics calculations via machine-learning techniques [5].

X-ray multiphoton ionization

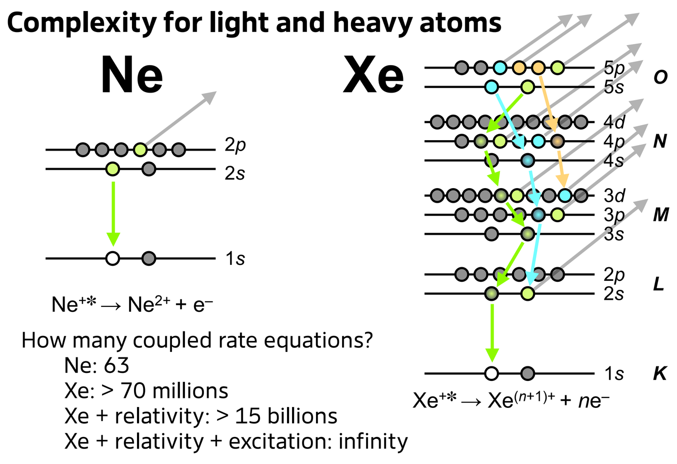
Interaction of matter with intense XFEL pulses is characterized by sequential multiphoton multiple ionization dynamics.

- Sequence of K-shell ionization (P), Auger-Meitner decay (A), and fluorescence (F)
- Extremely complicated ionization dynamics
- Highly excited electronic structure involved
- No standard quantum chemistry code available

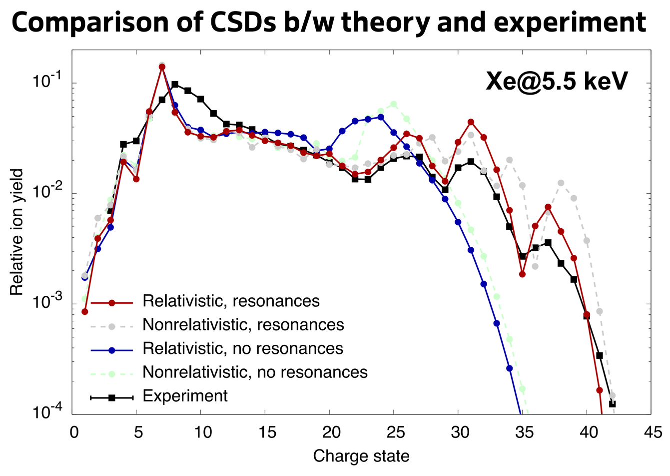
We implement an integrated toolkit, **XATOM** [6], to treat x-ray multiphoton ionization dynamics, based on rate-equation approach, within a consistent theoretical framework of nonrelativistic quantum electrodynamics, perturbation theory, and the Hartree–Fock–Slater model.

XRAYPAC:
a software package for modeling x-ray-induced dynamics of matter,
https://www.desy.de/~xraypac/

Complexity for light and heavy atoms



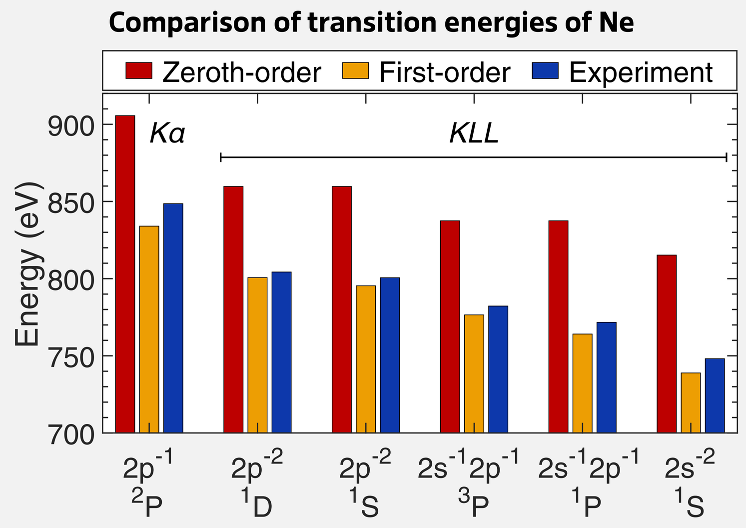
Comparison of CSDs b/w theory and experiment



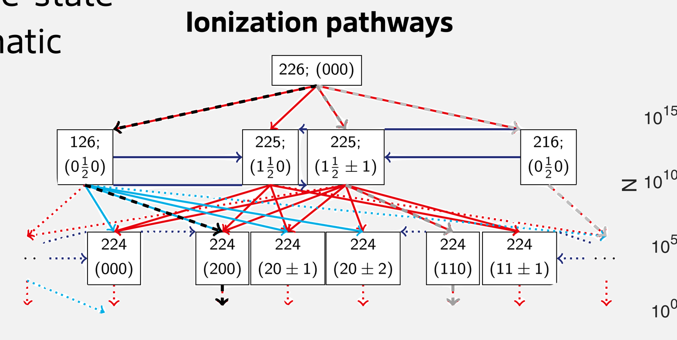
State-resolved XATOM

- First-order many-body perturbation theory to improve HFS calculations [1]
- Electronic configuration ($1s^{n1}2s^{n2}2p^{n3}$...) + quantum number (L, S, M_L, κ)
- X-ray ionization dynamics following quantum-state populations, rather than electronic configuration populations
  ➔ N of rate equations explodes
  ➔ Monte Carlo on-the-fly approach
- Almost no difference in charge-state distributions (CSDs), but dramatic improvement on photon and electron spectra [2]

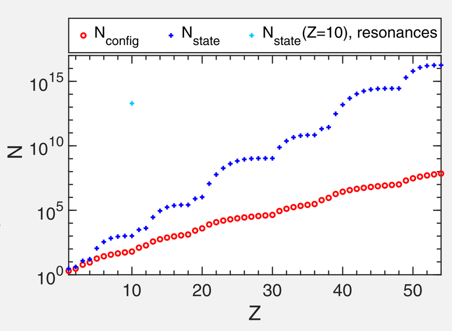
Comparison of transition energies of Ne



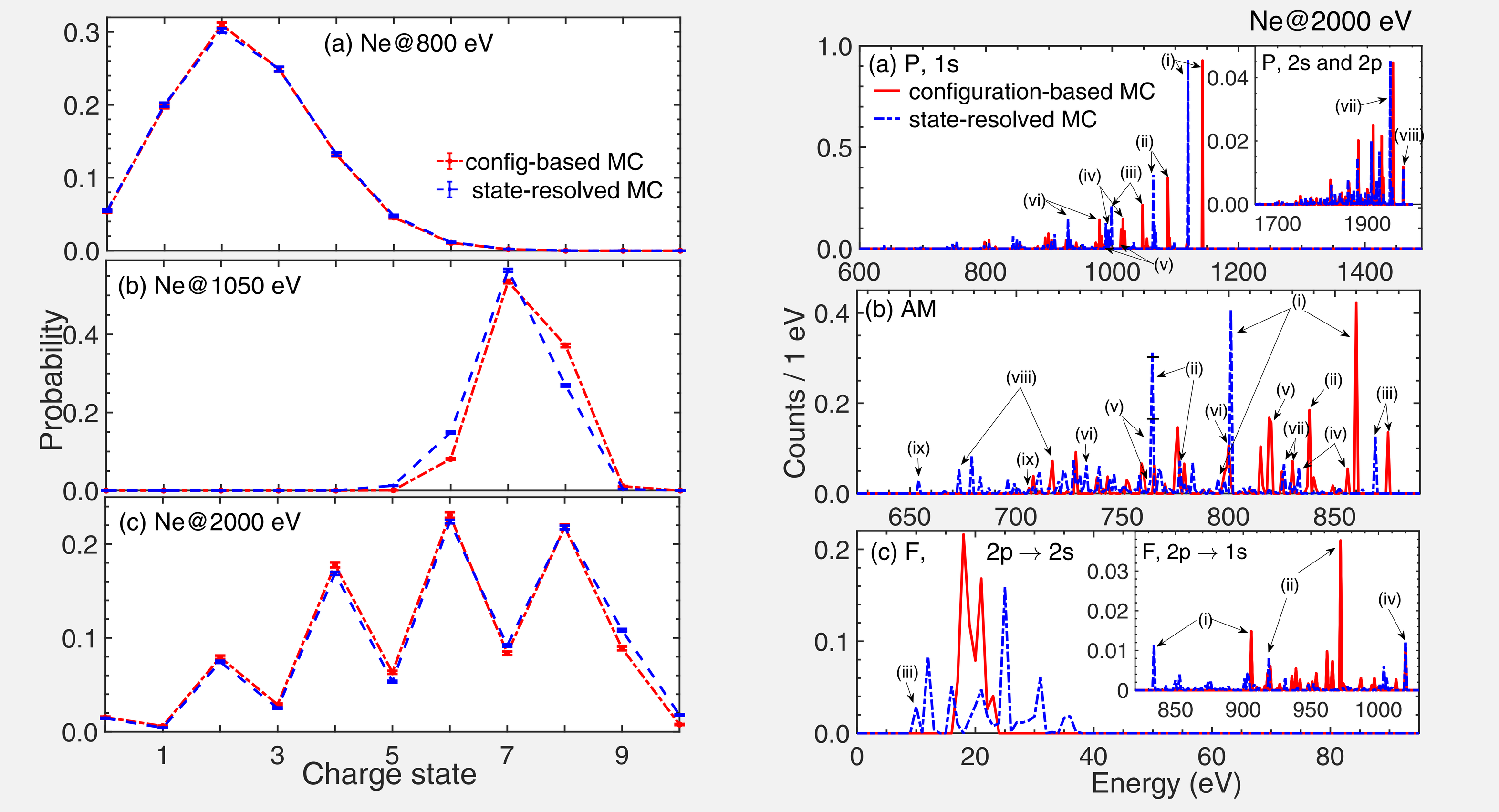
Ionization pathways



Computational complexity



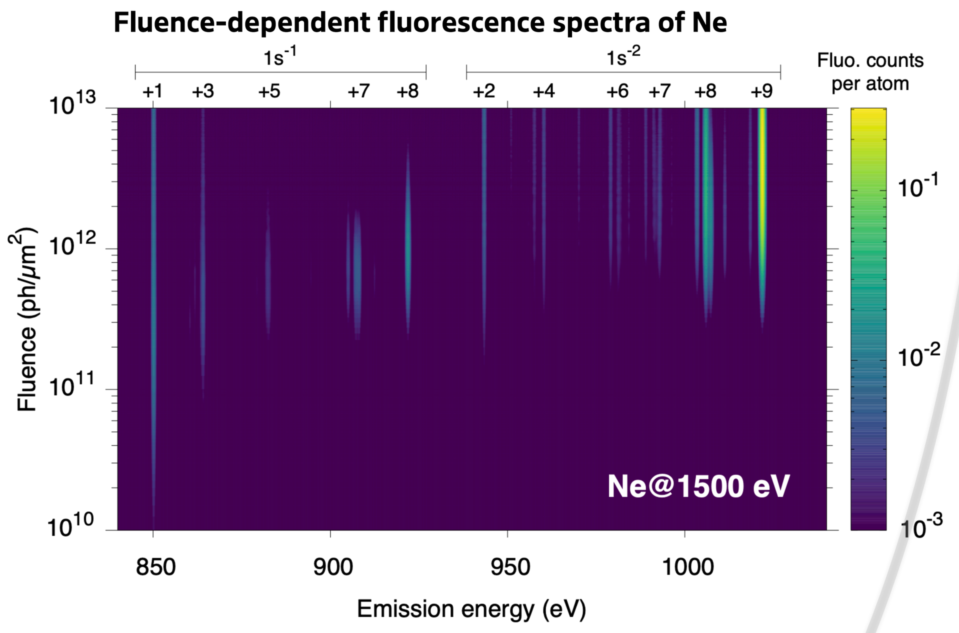
Comparison between config-based XATOM and state-resolved XATOM:
Ne CSDs [left panels] and spectra [right panels] of photoelectron (P), Auger-Meitner electron (AM), and fluorescence (F)



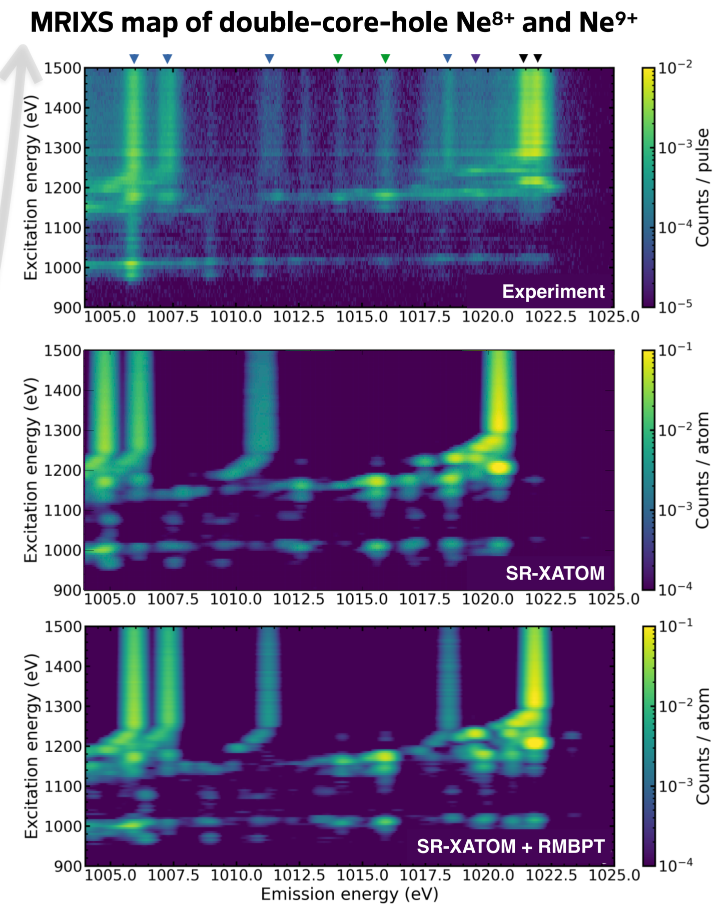
Multi-Resonant X-ray spectroscopy of Ne at European XFEL

- Fluorescence spectra of Ne as a function of incident photon energy measured at European XFEL [3]: RIXS (resonant inelastic X-ray scattering) or RXES (resonant X-ray emission spectroscopy)
- Two-dimensional RIXS map shows complex ionization dynamics involving multiple resonances
- State-resolved XATOM calculations reveal ionization mechanisms in unprecedented detail

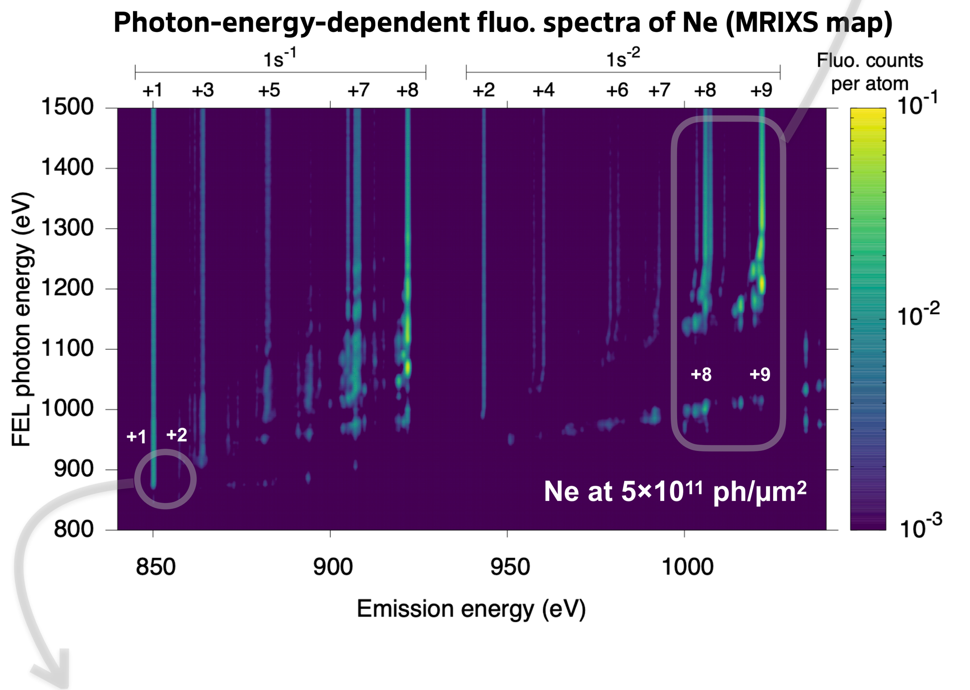
Fluence-dependent fluorescence spectra of Ne



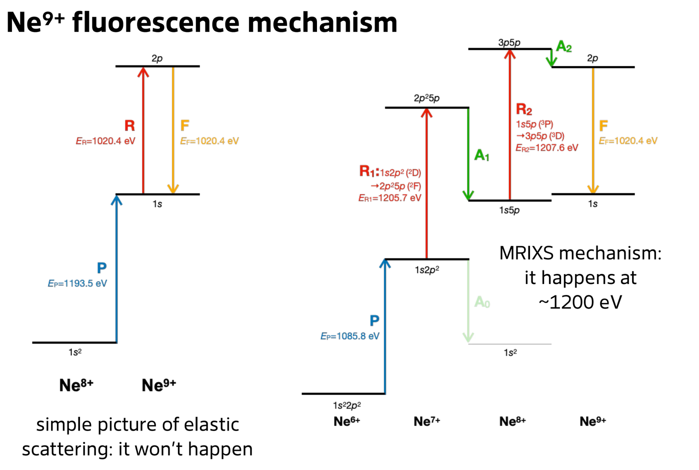
MRIXS map of double-core-hole Ne⁸⁺ and Ne⁹⁺



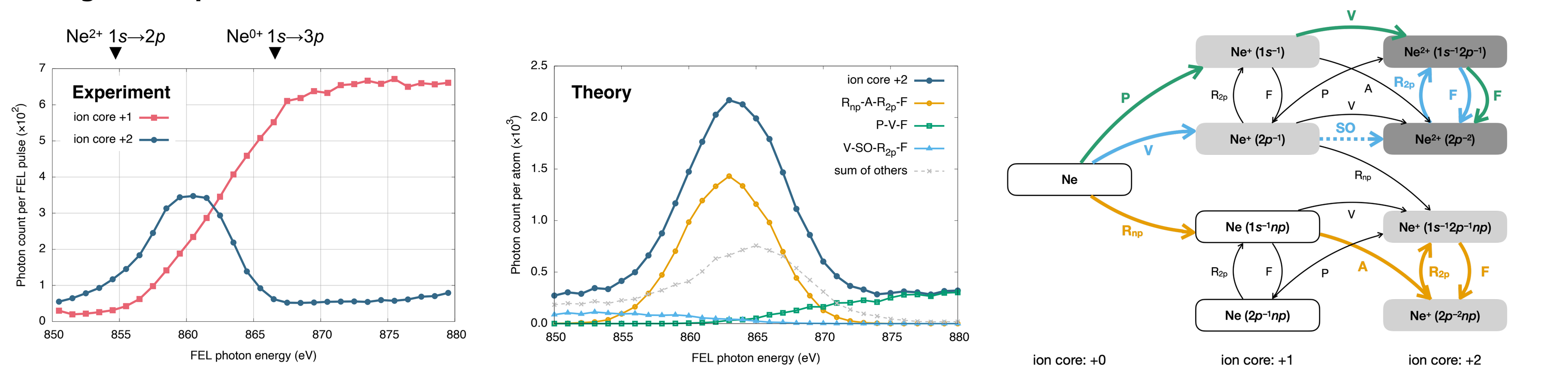
Photon-energy-dependent fluo. spectra of Ne (MRIXS map)



Ne⁹⁺ fluorescence mechanism



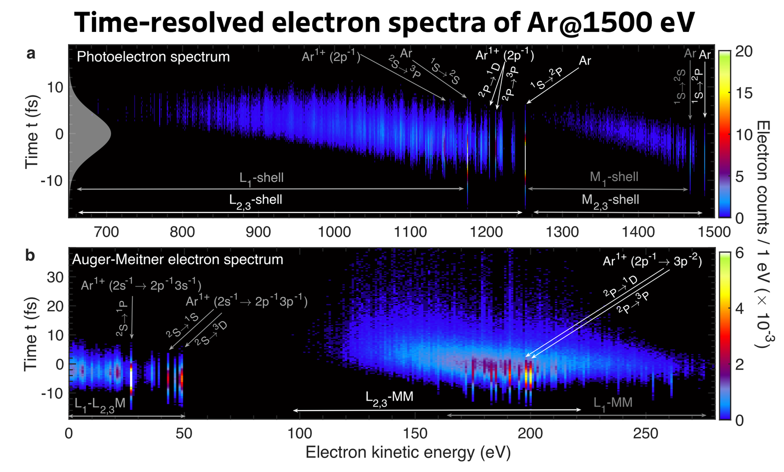
Emergence of pseudo-resonance in Ne²⁺ fluorescence

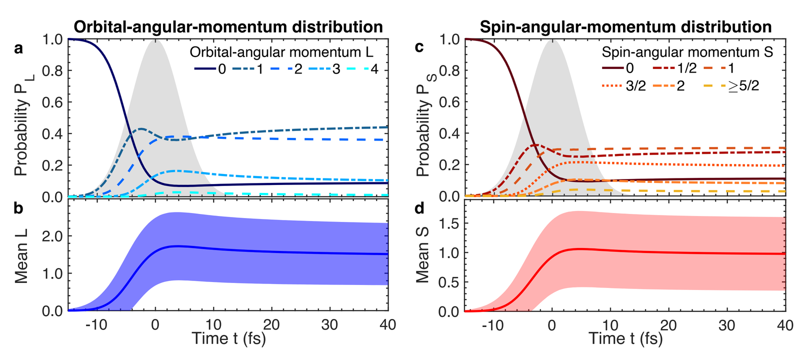


Orbital alignment dynamics

Time evolution of the electron-cloud alignment of Ar ions induced by intense XFEL pulses [4]

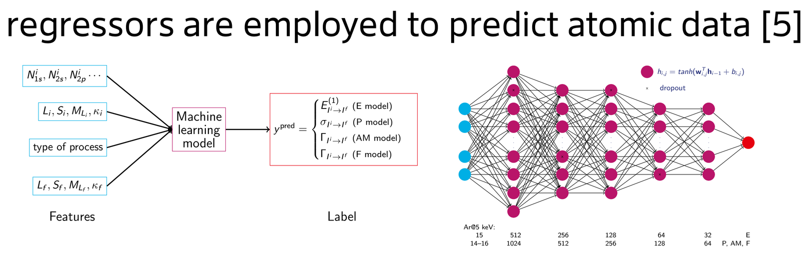
Time-resolved electron spectra of Ar@1500 eV



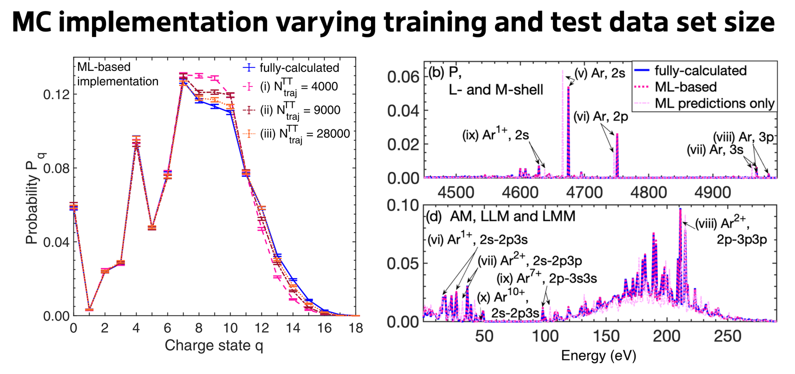


Machine-learning XATOM

Feedforward neural networks and random forest regressors are employed to predict atomic data [5]



MC implementation varying training and test data set size



Conclusions

- XATOM: enabling tool for studying x-ray multiphoton ionization dynamics
- XATOM has been extended to study quantum-state-resolved ionization dynamics
- First-order many-body perturbation theory improves accuracies of transition energies, which are critical for electron and photon spectra
- SR-XATOM explains new findings in Ne experiment at European XFEL: pseudo-resonance and multi-resonant inelastic x-ray scattering
- With SR-XATOM, we predict the existence of non-trivial electron-cloud alignment dynamics during intense XFEL pulses
- ML-based state-resolved MC implementation helps to reduce computational cost

References

[1] L. Budewig, S.-K. Son, and R. Santra, *Phys. Rev. A* **105**, 033111 (2022).
[2] L. Budewig, S.-K. Son, and R. Santra, *Phys. Rev. A* **107**, 013102 (2023).
[3] T. Baumann, S.-K. Son, J.-E. Rubensson, *et al.*, in preparation.
[4] L. Budewig, S.-K. Son, and R. Santra, (submitted).
[5] L. Budewig, S.-K. Son, Z. Jurek, M. M. Abdullah, M. Tropmann-Frick, and R. Santra, *Phys. Rev. Res.* **6**, 013265 (2024).
[6] Z. Jurek, S.-K. Son, B. Ziaja, and R. Santra, *J. Appl. Cryst.* **49**, 1048 (2016).

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