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Simulating Higher Harmonic Generation with Gaussian Basis Sets

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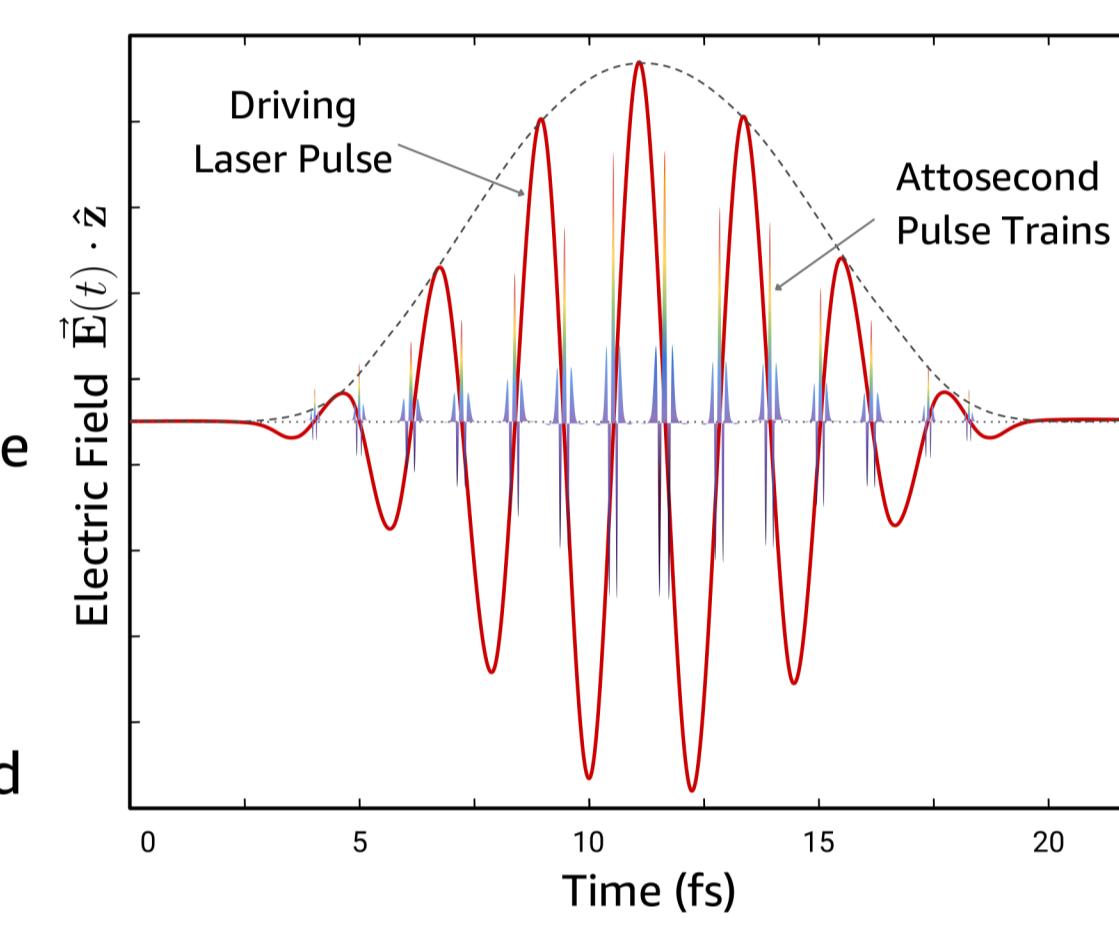
About this item

- Generating attosecond pulses is the crucial first step to achieving the grand goal of attosecond science: "control material processes at the level of electrons."
- Higher harmonic generation (HHG) is the only technique to provide coherent sub-femtosecond to a few hundred attosecond table-top sources of XUV and soft X-ray radiation. Further, analysis of the HHG spectra offers insights into correlated electron dynamics and forms the basis for attosecond spectroscopy. Interpretation of the underlying electron dynamics still remains to be extremely challenging.
- Therefore, the development of more accurate theoretical methods in tandem with experimental progress is indispensable for gaining new insights.

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Higher Harmonic Generation

- When an intense short-pulse laser interacts with matter, the target responds nonlinearly and emits coherent radiation at higher harmonic frequencies of the driving laser pulse.
 - Theoretically, HHG spectra can be obtained by a Fourier transform of the time-dependent induced dipole velocity,
- $$I_{\text{HHG}}(\omega) = \left| \frac{1}{t_f - t_i} \int_{t_i}^{t_f} dt \langle \mu(t) \rangle e^{-i\omega t} \right|^2.$$
- For decades, HHG has been studied using semi-classical models that employ many approximations, and fail to include key quantum effects.
 - Recently, L^2 -integrable Gaussian basis sets were shown to be efficient for simulating laser-driven electron dynamics. They have surpassed grid-based numerical methods, due to better computational scaling for multi-electron systems.
 - Here, hybrid Gaussian basis sets are prepared to simulate HHG for a single helium atom. Further, special functions are optimized and added to get a better description of continuum states and bound Rydberg states.


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Theoretical Specifications

Configuration Interaction (CI)	Any arbitrary N-electronic wave function can be expressed exactly as a linear combination of all possible Slater determinants formed from a complete set of one-electron orbitals. $ \Phi_{\text{CI}}\rangle = c_0 \Psi_0\rangle + \sum_{a,r} c_a^r \Psi_a^r\rangle + \sum_{a \leq b, r \leq s} \Psi_{ab}^r\rangle + \dots$
Gaussian Basis Sets	We use a combination of augmented Dunning basis sets (aug-cc-pVZ) with diffuse Gaussian-type orbital (GTO) functions. The exponents for these 'Kaufmann functions' for a particular angular momentum (l) are represented by a series, $a_{n,l} = \frac{1}{4(an + b_l)^2}$.
Time Propagation Scheme	We solve the time-dependent Schrödinger equation, $i\frac{\partial}{\partial t} \Phi_{\text{CI}}(t)\rangle = \left(\hat{H}_0 - \hat{r} \cdot \vec{E}(t)\right) \Phi_{\text{CI}}(t)\rangle$ using the Split-Operator technique: $\Phi(t+\Delta t) = [\mathbb{U}^\dagger \cdot e^{i\hat{r} \cdot \vec{E}(t)\Delta t} \cdot \mathbb{U}] e^{-i\hat{H}_0\Delta t} \Phi(t)$, where \mathbb{U} is the unitary transformation describing the change to energy eigen vector basis and $\vec{E}(t) = \vec{E}_0 \sin(\omega_0 t) f(t)$.
Lifetime Models	To avoid unphysical reflections of the wavefunction and to remedy the incomplete description of continuum states, we implement a heuristic lifetime model for all states $E_k^{\text{CI}} \geq E_0^{\text{CI}} + I_p$, such that $E_k^{\text{CI}} \rightarrow E_k^{\text{CI}} - i\Gamma_k$. Where Γ_k is the ionization rate (or inverse lifetime), calculated as $\Gamma_k^{\text{CISD}} = \sum_{a,r} (C_{a,k}^r ^2 \gamma_r + C_{aa,k}^r ^2 2\gamma_r) + \sum_{a,r,s} C_{aa,k}^s ^2 (\gamma_r + \gamma_s) + \sum_{a \leq b, r} C_{ab,k}^r ^2 2\gamma_r + \sum_{a \leq b, r \leq s} (A C_{ab,k}^s ^2 + B C_{ab,k}^s ^2) (\gamma_r + \gamma_s)$. Here, $\gamma_r = 1/\tau_r = \Theta(\varepsilon_r) \sqrt{2\varepsilon_r}/dr$ is the ionization rate calculated for a virtual orbital (r), with an empirical parameter d_r .

User question & answers

- ▲ Question : How are these hybrid basis functions prepared and optimized?
1 Votes Answer : Using AVQZ as a core, different basis sets are prepared by adding K-functions systematically, varying number of shells N , maximum angular momentum l_{max} , and c such that $N_{k_l} = N - k_l c$. For a particular atom, the Gaussian exponents are optimized by minimizing the ground state energy as a function of parameters a_i and b_i .
- ▲ Question : What are the laser parameters used in this study?
1 Votes Answer : All HHG spectra here are computed using a cosine-squared pulse ($f(t) = \cos^2(\pi(t - \sigma)/2\sigma)$ for $|t - \sigma| \leq \sigma$) of carrier frequency 1.55 eV (800nm) and pulse width of 54 fs. Can confirm, that they at least have results for Helium atom with laser intensities: 2×10^{14} , 3×10^{14} and $5 \times 10^{14} \text{ W/cm}^2$ (corresponding Keldysh parameters $\sqrt{I_p/2U_p}$: 1.01, 0.83, and 0.63).
- ▲ Question : Can I simulate HHG for molecules? What about ab initio lifetime?
1 Votes Answer : Yes, it is possible to simulate HHG for small molecules like dihydrogen using floating Gaussian functions (at ghost atom centers). Currently, ab initio lifetimes are only available for atoms, but you can use the heuristic models and tune your parameters for good results.

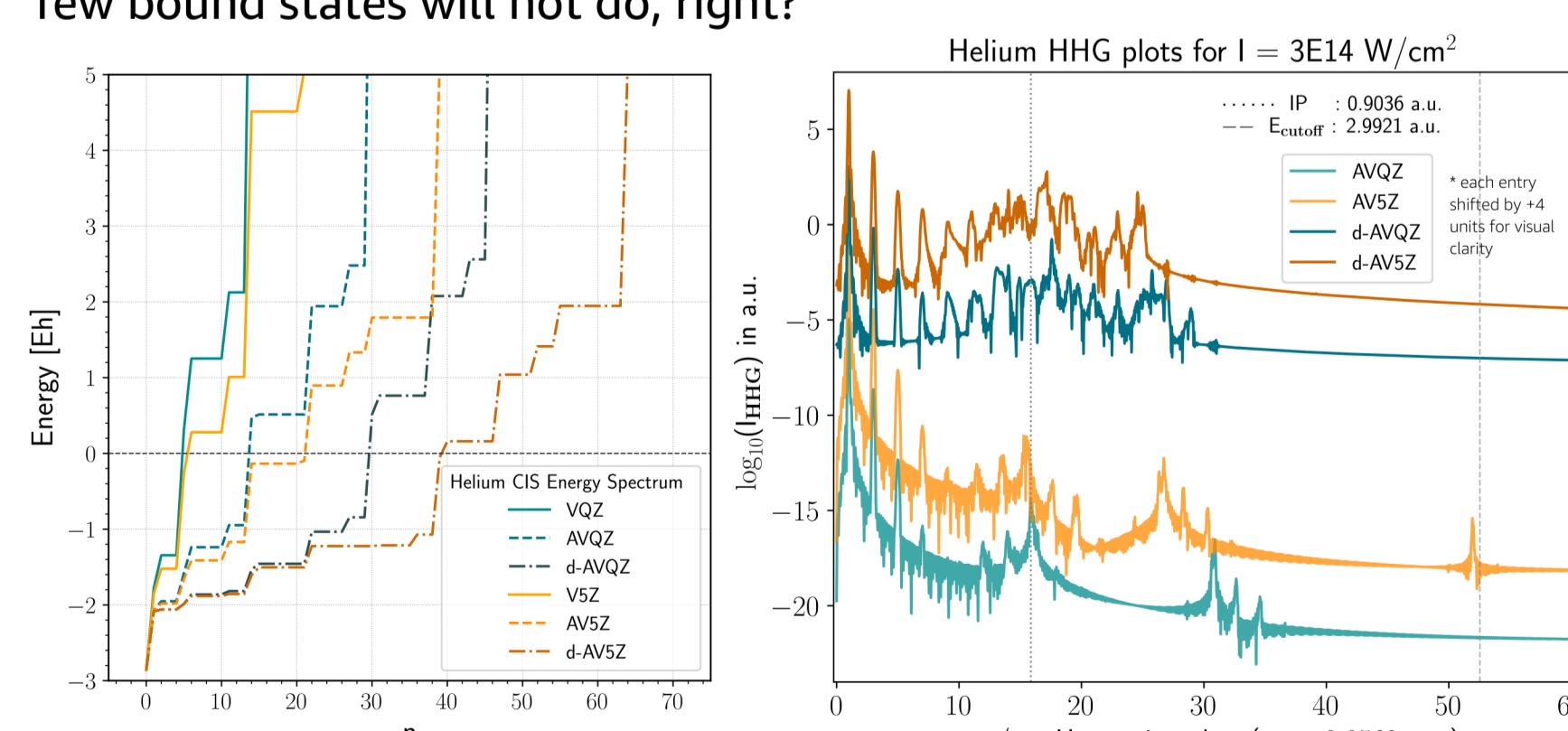
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Chattur Ramalingam

 No higher harmonics! I want my money back
Dunning Basis Sets | Verified analysis

This is a fraud. Now tell me, how will you get an HHG spectrum without good Rydberg and continuum states? Just a few bound states will not do, right?



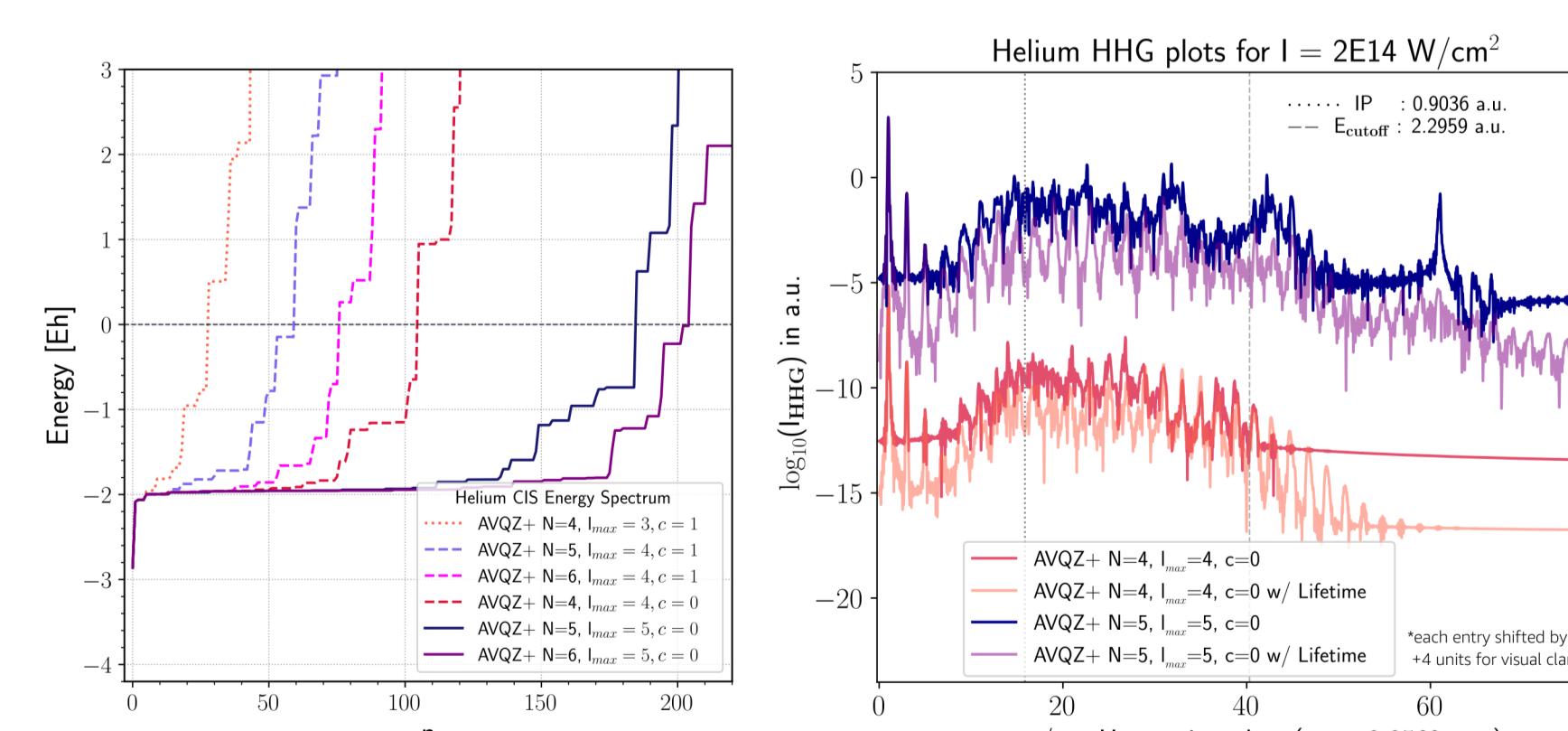
Prof. Viru S. Bhudde

Ok HHG spectrum, can do better.

AVQZ + N={4, 5, 6}, lmax={3,4,5}, c={0,1} | Verified analysis

Pros: Basis sets with same no. of angular momentum functions in all shells ($c=0$) give sufficient bound states and perform better. Further, adding too many diffuse functions can be counter-productive.

Cons: Still too large for a one-electron basis, to compute the Full CI Hamiltonian matrix and study exact dynamics.

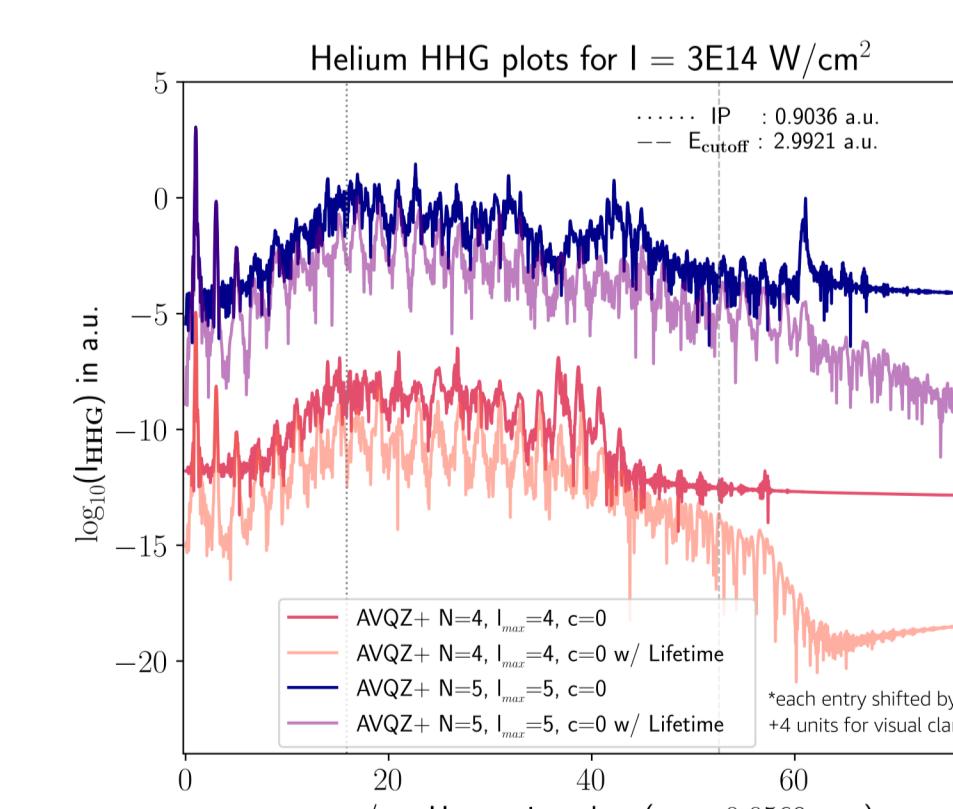


Phunsukh Wangdu

If you can afford it, go for Full CI/AVQZ+440.

aug-cc-pvzx + N=6, lmax={3,4,5}, c={0,1} | Verified analysis

It might be expensive but, try FCI/AVQZ+440 level of theory. This will allow you to study the many-electron effects neglected in other theories. But, watchout for any convergence issues with very high intensities.



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