Electronic Dynamics of Atoms and Molecules Beyond the Electric Dipole Approximation in the presence of Strong Laser

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1. Introduction

- **Electric Dipole Approximation**
  When the wavelength of the laser field is much larger than the dimensional extent of the atomic/molecular system, the spatial dependence of the laser field can be ignored.

  Mathematically, the Electric field of the electromagnetic wave is represented as $\vec{E}(\vec{r},t) = E_o\cos(\vec{k}.\vec{r} - \omega t)\hat{\epsilon}$. We can approximate the complex exponential as,

$$e^{i\vec{k}.\vec{r}} = 1 + i\vec{k}.\vec{r} + \ldots \qquad (1)$$

  When this expansion is approximated as unity, this corresponds to dipole approximation, wherein the electric field becomes $\vec{E}(\vec{r},t) = E_o\cos(\omega t)\hat{\epsilon}$.

- **Beyond the Electric dipole approximation**: When the additional correction terms in (1) is included in the Electric field/vector potential, we are going beyond the electric dipole approximation.
- Actual laser fields are **plane-wave (PW) fields** propagating in space and time.
- A free electron in a PW field describes a 'figure-8' motion.
- Electronic dynamics of **H and He atom** and $\mathbf{H_2O}$ **molecule** is studied **beyond the electric dipole approximation** in the presence of **linearly polarized laser pulse**.

2. Theory

A **length gauge Hamiltonian for beyond the electric dipole approximation** in the presence of **linearly polarized laser pulse** polarized along z-direction and propagating along the x-direction as derived by Selstø and Førre [1] is of the form (in atomic units),

$$\mathrm{H_{ND}} = \frac{p^2}{2} + V(\vec{r}) + E(x,t)z + \frac{1}{2}\left[\left\{z\,\frac{\partial A(x,t)}{\partial x}\right\}^2 - z\left\{p_x\frac{\partial A(x,t)}{\partial x} + \frac{\partial A(x,t)}{\partial x}\,p_x\right\}\right]$$

Taking the form of the vector potential as $A(x,t) = A_o\cos(kx - \omega t)$ implies Hamiltonian $\mathrm{H_{ND}}$ becomes,

$$\mathrm{H_{ND}} = \frac{p^2}{2} + V(\vec{r}) - E_o\sin(kx-\omega t)\,z - \frac{E_o^2}{4c^2}\Big\{\cos(2(kx-\omega t))\Big\}z^2 + \frac{E_o^2}{4c^2}z^2 + \frac{E_o}{2c}z\,p_x\Big\{\sin(kx-\omega t)\Big\} + \frac{E_o}{2c}z\Big\{\sin(kx-\omega t)\Big\}p_x \qquad (2)$$

3. (t,t') method of time-propagation

- Method developed by U. Peskin and N. Moiseyev [2].
- Introduction of a new t' coordinate in an extended Hilbert space as suggested by Sambe and Howland.
- TDSE becomes

$$i\hbar\left[\frac{\partial}{\partial t} + \frac{\partial}{\partial t'}\right]\Psi(\vec{r},t,t') = \hat{H}(\vec{r},t')\Psi(\vec{r},t,t')$$

  which gives,

$$\Psi(\vec{r},t,t') = e^{-i/\hbar\hat{\mathcal{H}}_F(\vec{r},t')(t-t_o)}\Psi(\vec{r},t_o,t')$$

  where $\hat{\mathcal{H}}_F = \left[\hat{H}(\vec{r},t') - i\hbar\frac{\partial}{\partial t'}\right]$ resembles a Floquet-type operator in the t' coordinate.
- Eliminates the need for time-ordering operator.
- The physical solution $\Psi(\vec{r},t)$ is extracted from full solution $\Psi(\vec{r},t,t')$ at $t = t'$.

References

[1] S. Selstø and M. Førre. Alternative descriptions of the light-matter interaction beyond the dipole approximation. *Phys. Rev. A*, 76(023427), 2007.

[2] U. Peskin and N. Moiseyev. The solution of the time-dependent schrödinger equation by the (t,t′) method: Theory, computational algorithm and applications. *J. Chem. Phys.*, 99:4590–4596, 1993.

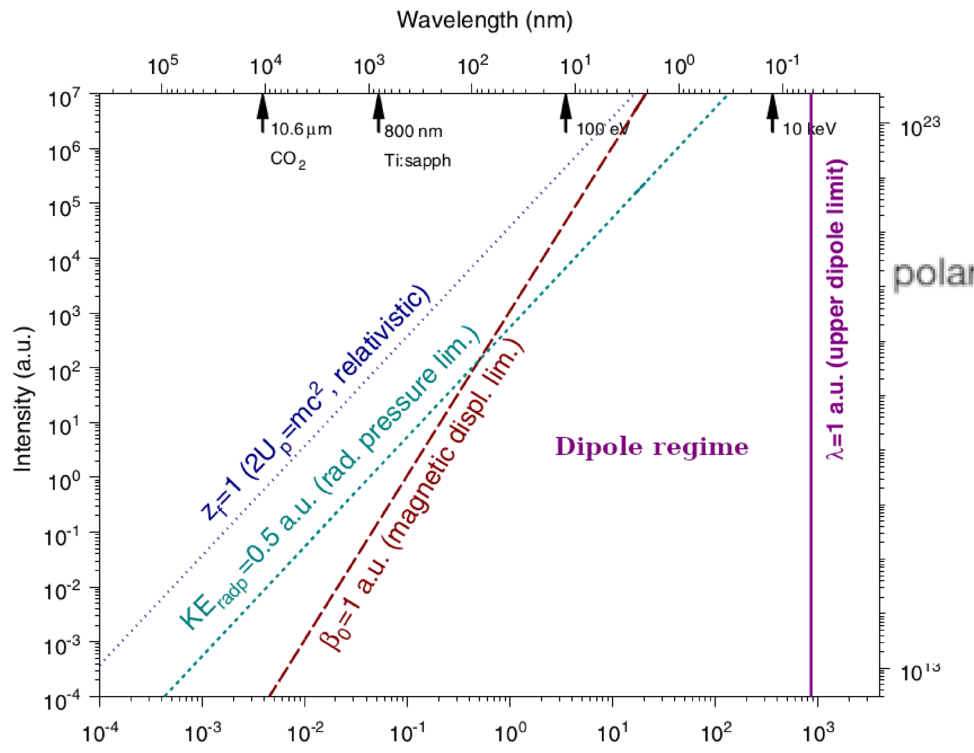
[3] Prashant Raj, Alkit Gugalia, and P. Balanarayan. Quantum dynamics with explicitly time-dependent hamiltonians in multiple time scales: A new algorithm for (t, t') and (t, t', t") methods in laser-matter interactions. *J. Chem. Theory Comput.*, 16:35–50, 2020.

[4] H. R. Reiss. The tunnelling model of laser-induced ionization and its failure at low frequencies. *J. Phys. B: At. Mol. Opt. Phys.*, 47(204006), 2014.

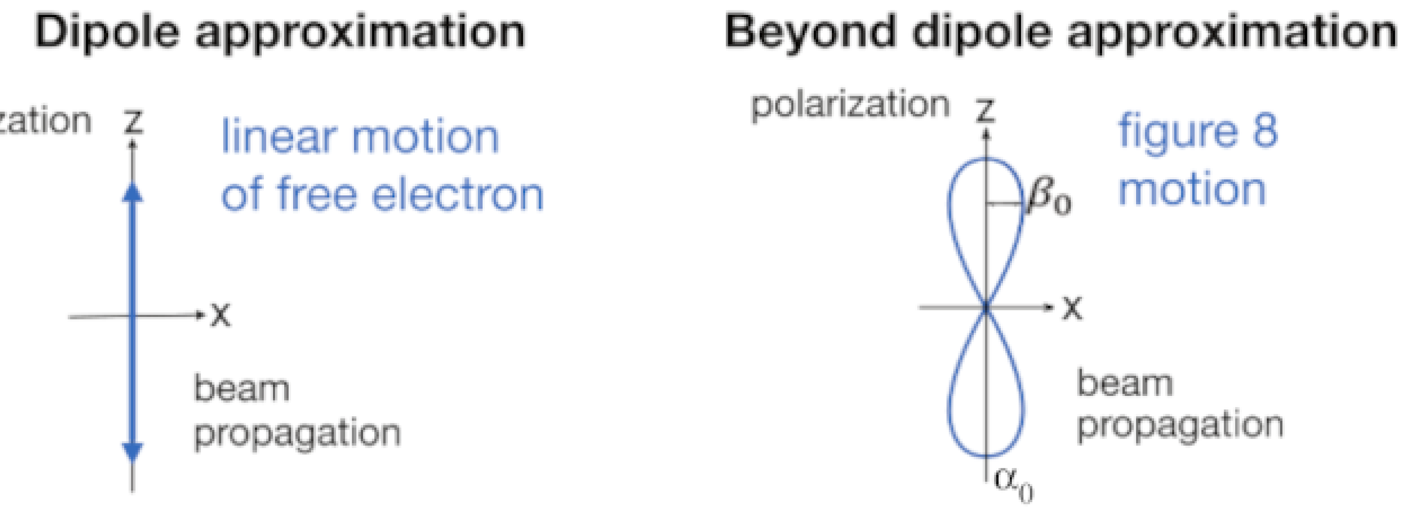
3. Methodology

- The non-dipole Hamiltonian matrix H_{ND} in (2) is constructed in a basis set of 3D-cartesian Gaussian-type basis functions.
- Using Gamess-US, initial free field coefficients of the systems are obtained in the Configuration Interaction level of theory.
- A new algorithm of (t, t') propagation method is used which gives a significant advantage by only having to store the matrices of the order of size of the coefficient matrix, hence giving drastic reduction in storage space required for the program [3].

4. Results and Observations

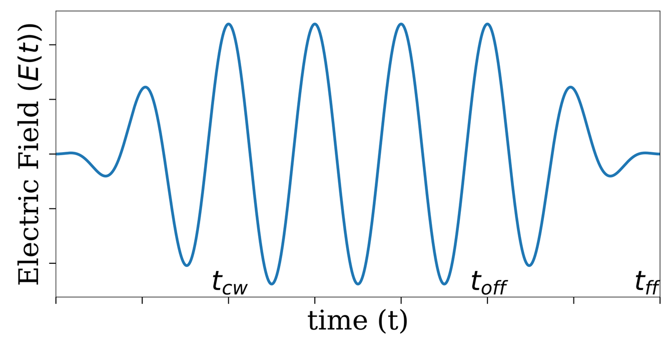


A free electron in a PW field describes a figure-8 motion



Form of the laser pulse

Linearly Polarized laser pulse
No. of optical cycles = 7



Lower limit of the dipole approximation [4]

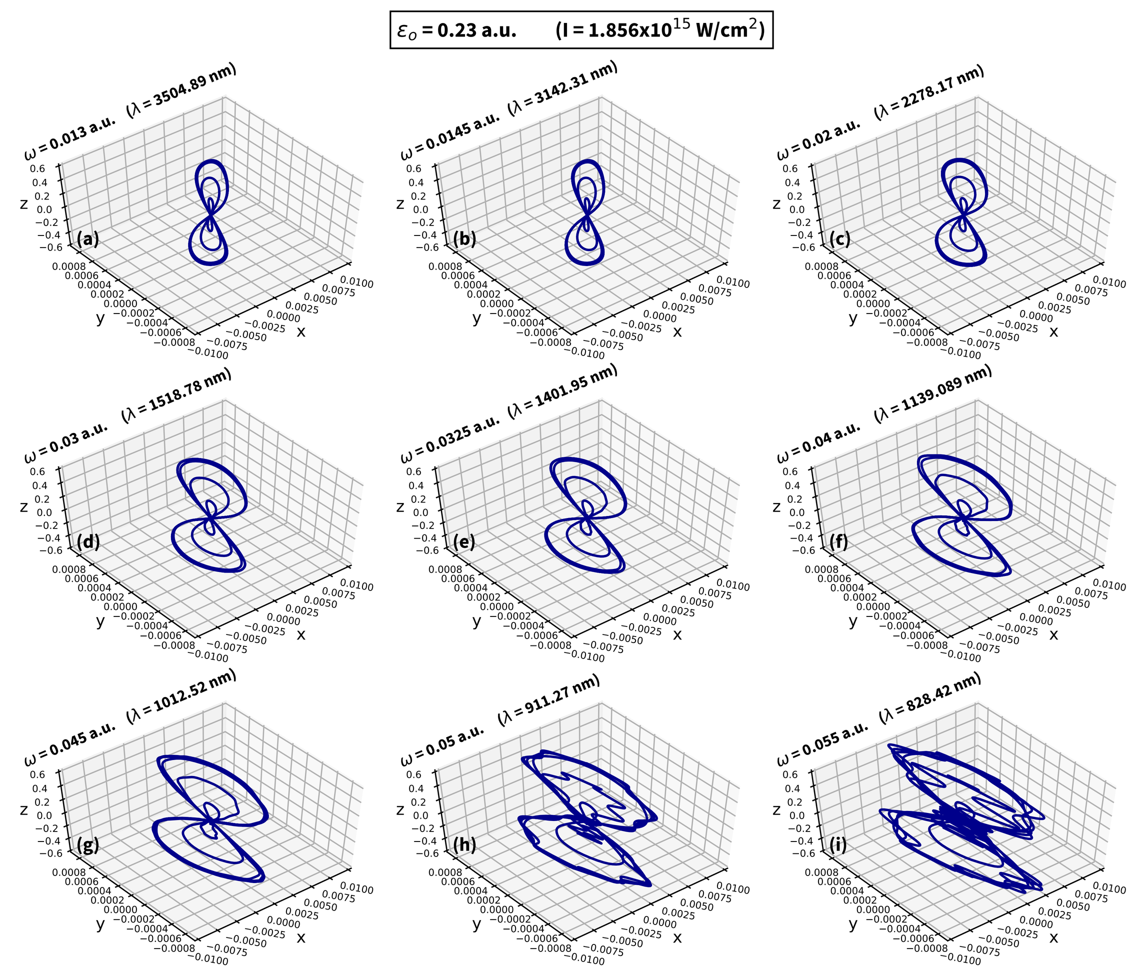
β_o =Amplitude of figure-8 motion along the beam propagation direction

$$\beta_o \approx \frac{U_p}{2mc\omega}.$$

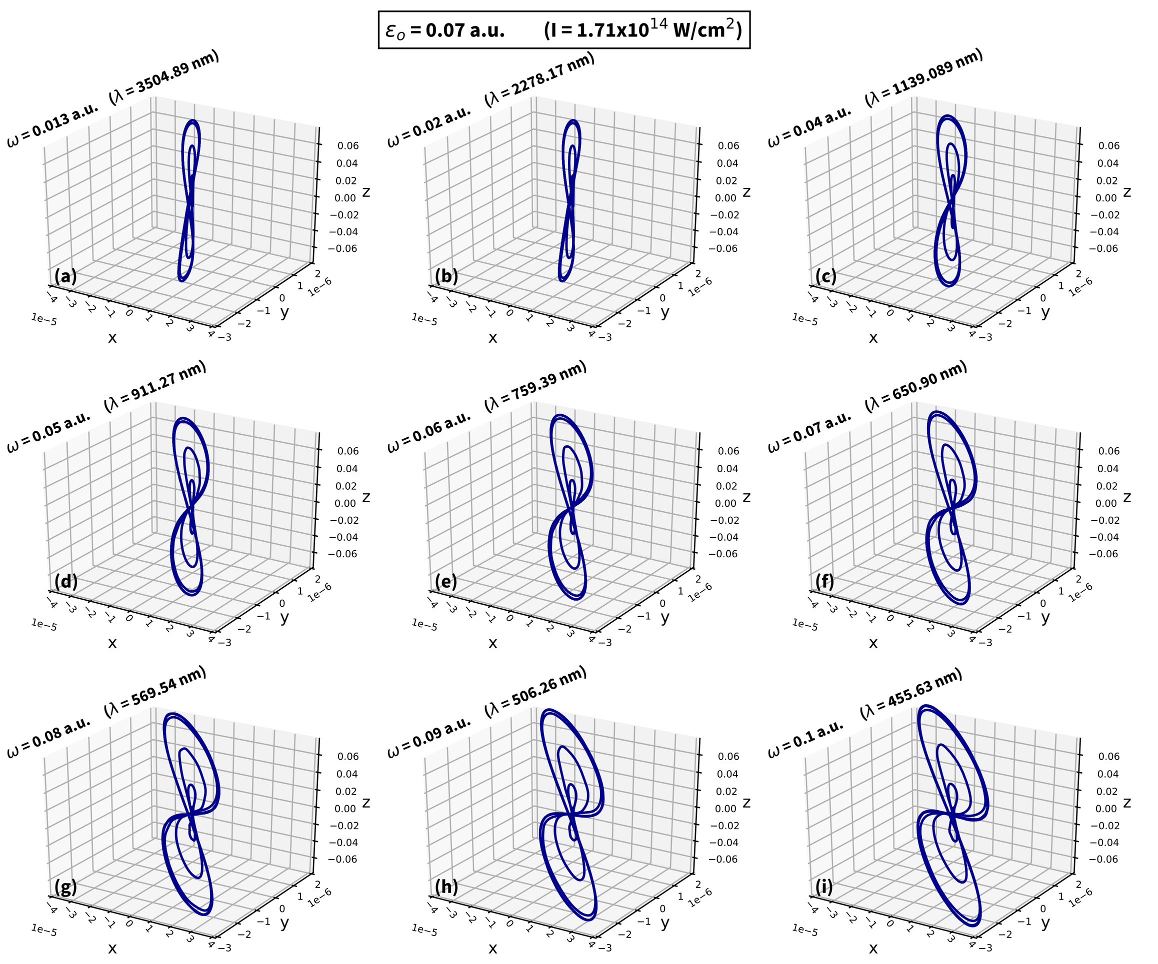
When $\beta_o \approx 1$ a.u., I = $8c\omega^3$

Total Non-Dipole induced dipole moment w.r.t. time

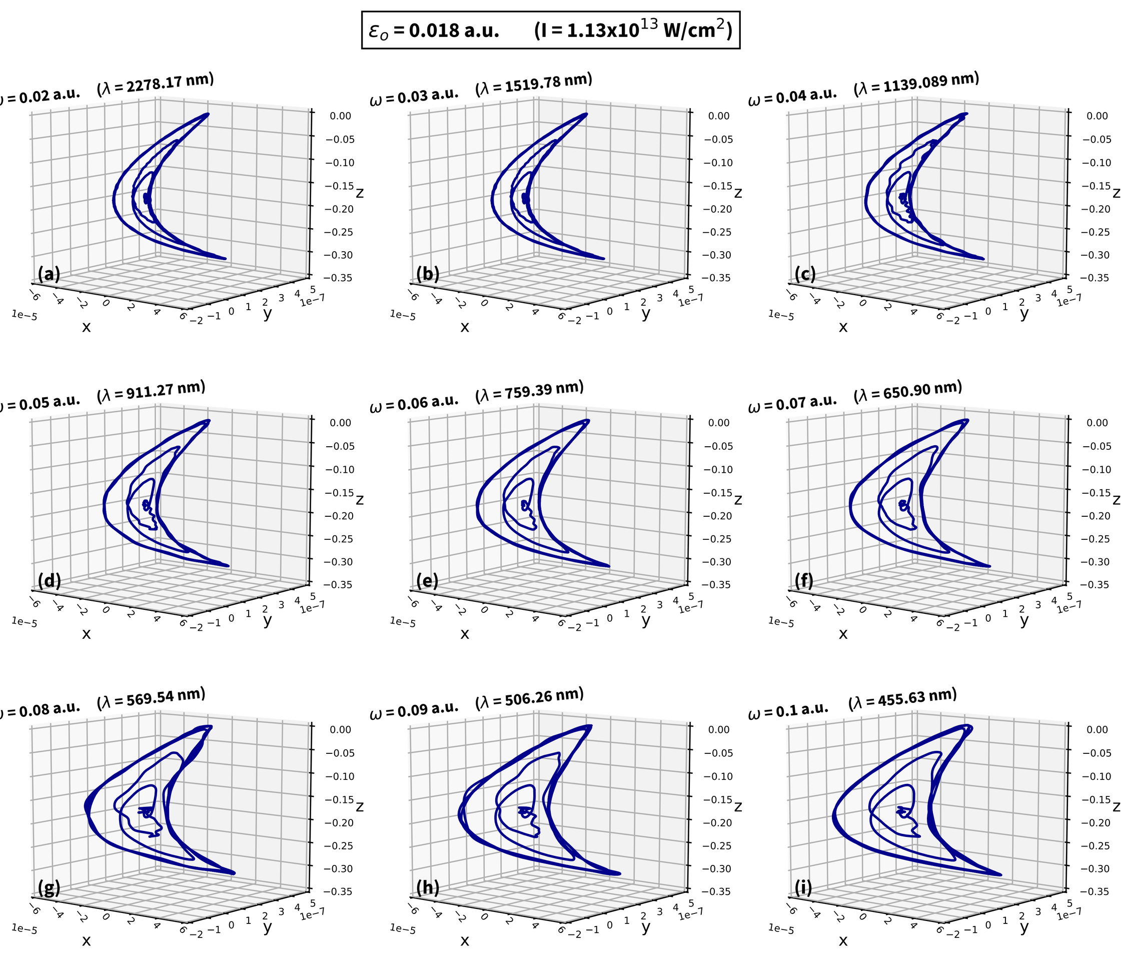
1) **H atom**; CI level of theory; 38 CSFs; COEMD-REF basis set



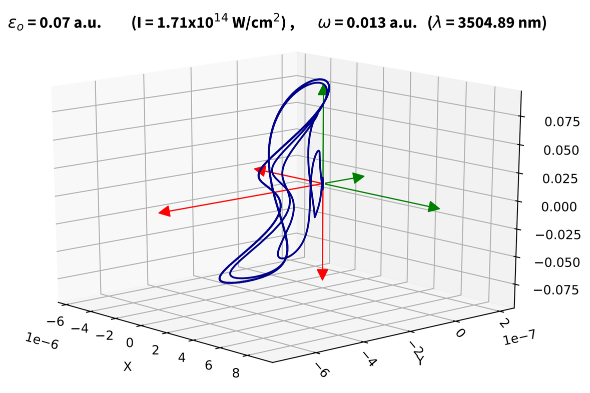
2) **He atom**; FCI level of theory; 741 CSFs; COEMD-REF basis set



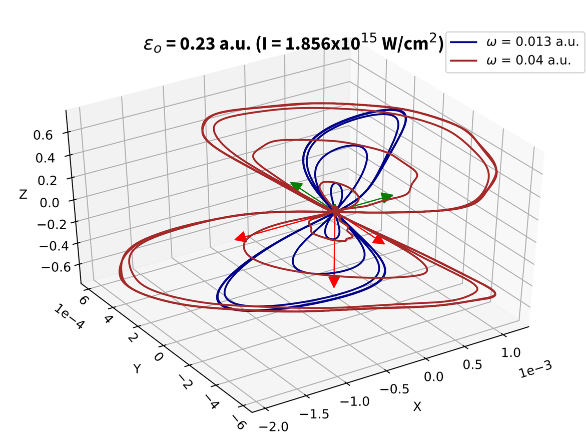
3) $\mathbf{H_2O}$ **molecule**; CIS level of theory; 191 CSFs; aug-cc-pVDZ basis set



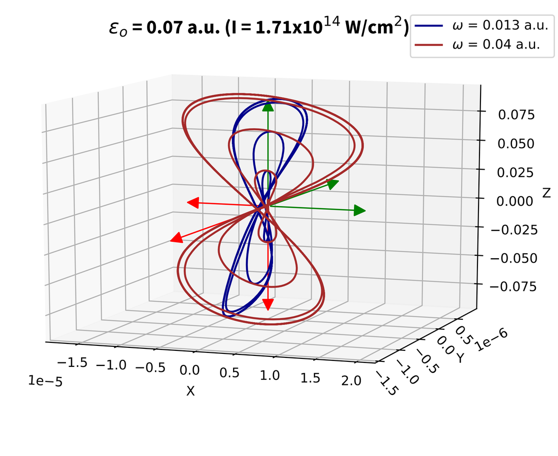
▸ He atom excursion



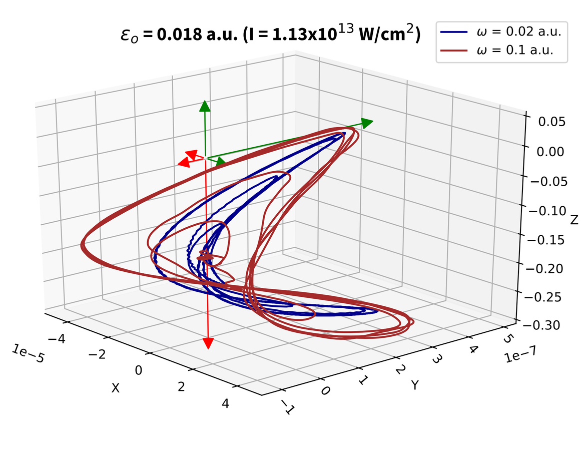
1) H atom



2) He atom



3) H_2O molecule



5. Conclusions

- The non-dipole induced dipole moment shows a **figure-8-motion** during the propagation of the laser pulse with its long axis along the laser polarization direction and short axis in the xy plane, where x being the propagation direction, for both **hydrogen and helium atom**.
- The non-dipole induced dipole moment in **Water molecule** gives a **peculiar paraboloid like structure**.
- In the particular case of **Helium atom**, at **low laser frequencies**, the figure-8 motion originates from origin, **traverses in the negative direction** in the xy-plane during the maxima of the laser electric field strength and returns back to origin.

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