TWO PHOTON ABSORPTION

A Test of Pseudo State Summations to Calculate Polarizability

Spencer Percy and G.W.F. Drake

University of Windsor

Overview

1. Two Photon Absorption

2. Perturbation theory and why we use Pseudostates

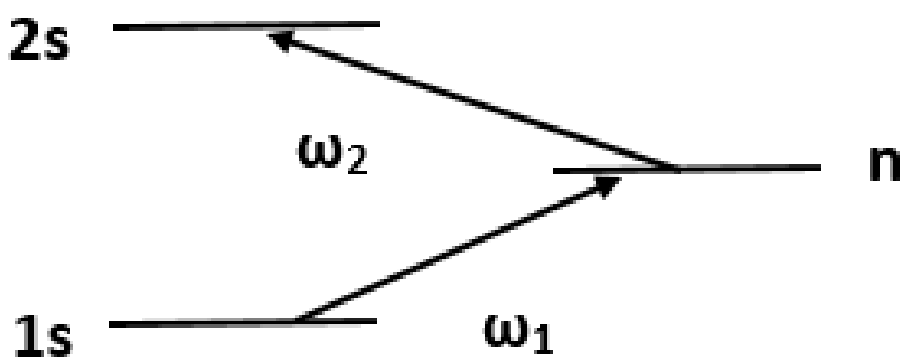
3. Variational Methods Example: The Polarizability of the 1s State of Hydrogen

Motivation

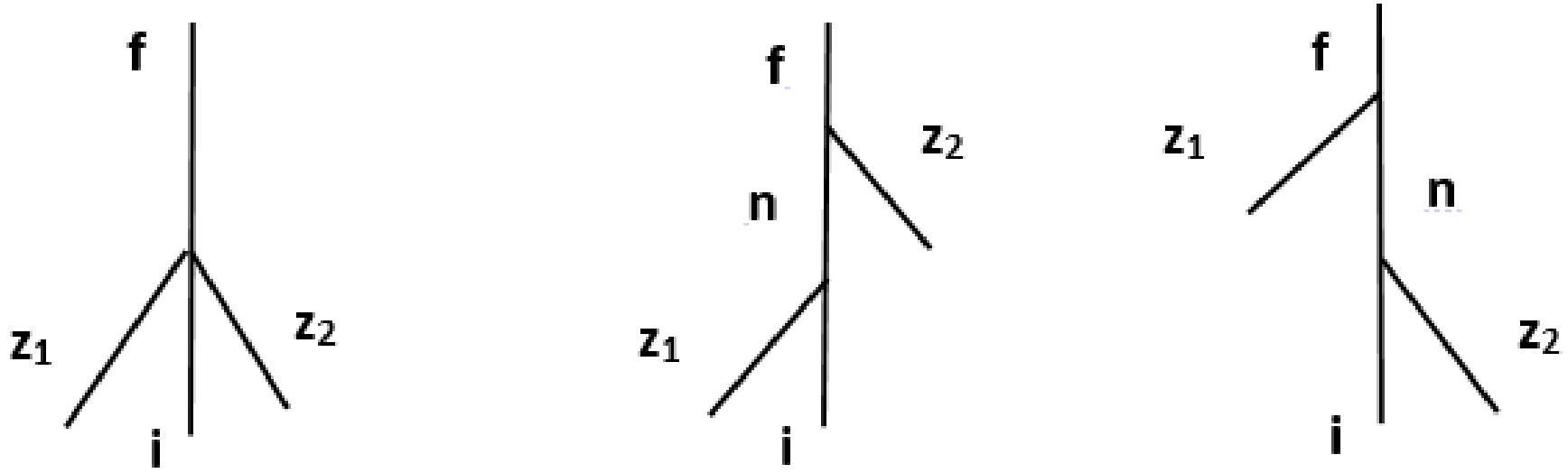
- 2s to 1s transitions with a single electric dipole photon are forbidden by parity. The dominant radiative decay mechanism is two-photon transitions. The 2s state lives for about 1/8 sec, which is a billion times longer than the neighboring 2p state
- Using lasers you are able to jump to a higher excited state using a lower frequency laser then the full transition would require
- Our group will be checking to see if the process could be a significant correction to astrophysical spectroscopy

Two Photon Absorption

- Defined as the simultaneous absorption of two photons
- Very similar in operation to scattering processes
- Two different frequency photons can be used as long as the sum of their frequencies is equal to the transition frequency of the given state



Summation Over States



Possible Transitions: Simultaneous absorption and absorbing one photon then the other

$$\sum_n \left(\frac{\langle f|z_2|n\rangle\langle n|z_1|i\rangle}{\omega_1 - \omega_n} + \frac{\langle f|z_1|n\rangle\langle n|z_2|i\rangle}{\omega_2 - \omega_n} \right)$$

Example: Polarizability of Hydrogen

- A very similar equation is found when calculating polarizability
- Defined as the second order perturbation energy due to an external field
- To calculate it you are required to sum over the bound states and then integrate over the continuum

$$\alpha_d = -2\sum_n \frac{\langle 1s|z|n\rangle\langle n|z|1s\rangle}{E_{1s} - E_n}$$

Example Cont'd

- For an external field $V = eFr\cos\theta$ the first order equation can be solved analytically

$$\Psi^{(1)} = -(1/3)(2r + r^2)e^{-r}Y_1^0(\hat{\boldsymbol{r}})$$

- Which satisfies the first-order perturbation equation

$$\left(H^{(0)} - E^{(0)}\right)\left|\Psi^{(1)}\right\rangle + eFz\left|\Psi^{(0)}\right\rangle = 0$$

- The first order energy $E^{(1)} = eF\left\langle\Psi^{(0)}\middle|z\middle|\Psi^{(0)}\right\rangle$ is zero by parity and thus not included

Example Cont'd

- The second order energy is given by $\boldsymbol{E^{(2)} = eF\langle \Psi^{(1)} | z | \Psi^{(0)} \rangle}$
- Instead of solving $\boldsymbol{\Psi^{(1)}}$ analytically we can multiply the first-order perturbation equation by the inverse operator $\boldsymbol{\left(H^{(0)} - E^{(0)}\right)^{-1}}$ to obtain the spectral representation of $\boldsymbol{\Psi^{(1)}}$

$$\left|\Psi^{(1)}\right\rangle = eF \sum_{n} \frac{\left|\Psi_n\right\rangle\left\langle\Psi_n\right| z \left|\Psi^{(0)}\right\rangle}{E^{(0)} - E_n}$$

- Where the sum over n represents the summation over the infinite bound states and integration over the continuum

Alternatively

- As an alternative to this lengthy summation we can instead insert a discrete variational set of pseudostates of the form

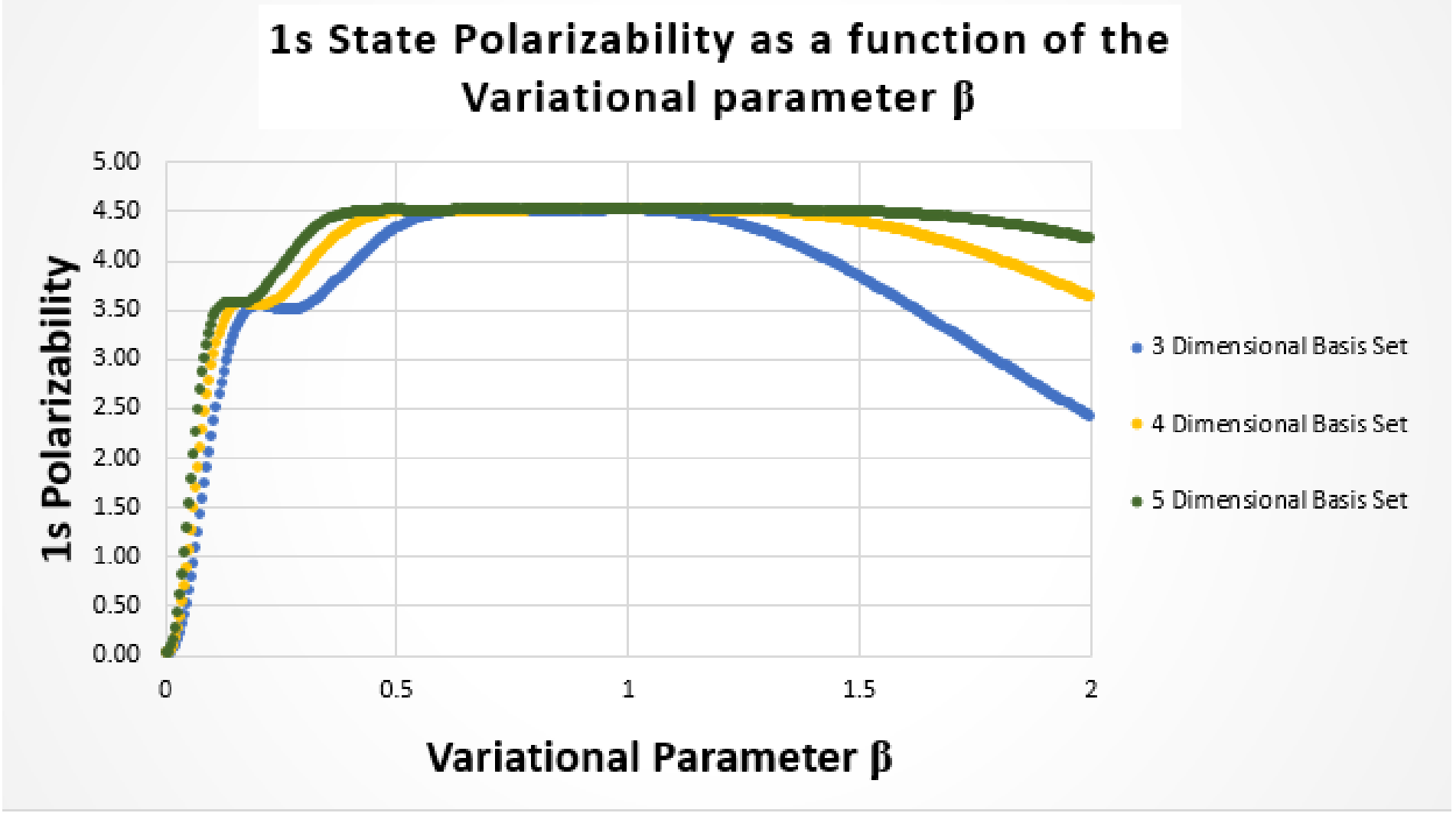
$$\tilde{X}_p = \sum_i c_i r^i e^{-\beta r} \cos\theta$$

- Where c_i are linear variational parameters found by diagonalizing the Hamiltonian in the generalized eigenvalue problem, β is our non-linear variational parameter and we multiply by $\cos\theta$ because for our example we need P-states

Convenience

- This method will give the exact analytic solution to $\Psi^{(1)}$ for a two term basis set when β=1
- Using this method with our example we can calculate the solution to the polarizability calculation to be $\alpha_d = 4.5a_0^3$ with a_0 being the Bohr radius
- In addition, one obtains a variational extremum at β = 1, as demonstrated by varying β and calculating the polarizability. The value obtained from pseudostates for arbitrary β is therefore a lower bound on the exact value. One can expect this also to be true in the two-electron case of helium where the exact analytic solutions are not known

Variational Methods



Thank you

- Group Members: GWF Drake, Daniel Venn, Ryan Peck, Eva Schulhoff, Jacob Manallo, Maha Sami, Aaron Bondy