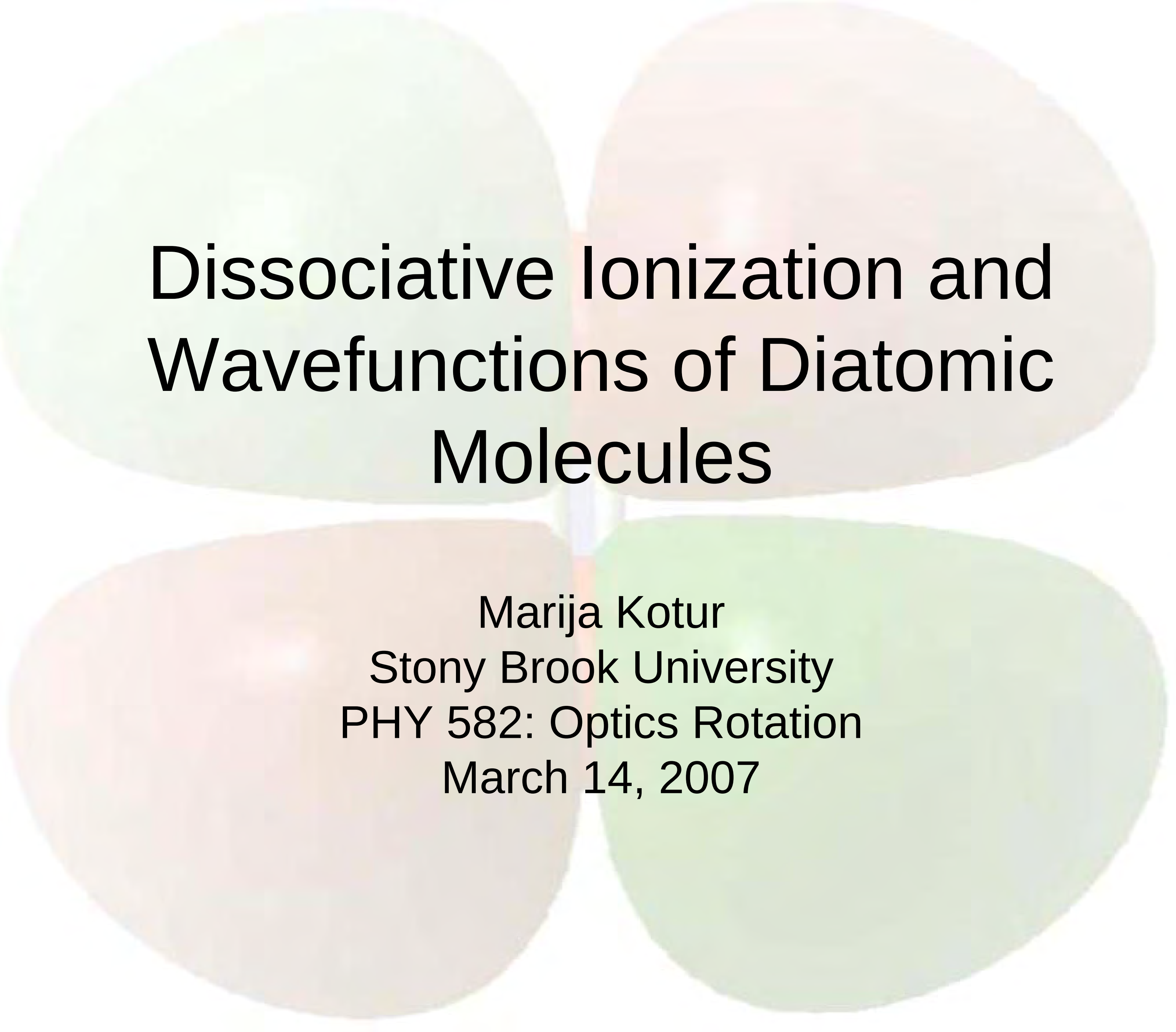

Dissociative Ionization and Wavefunctions of Diatomic Molecules

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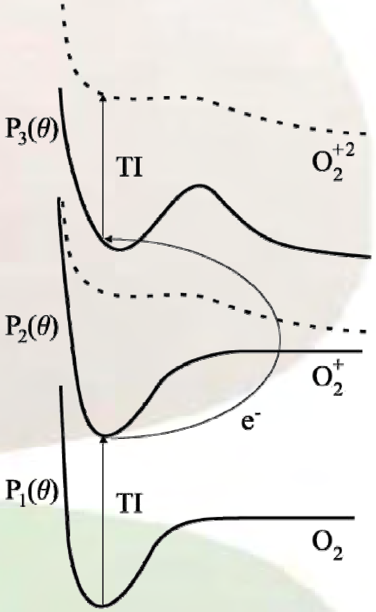
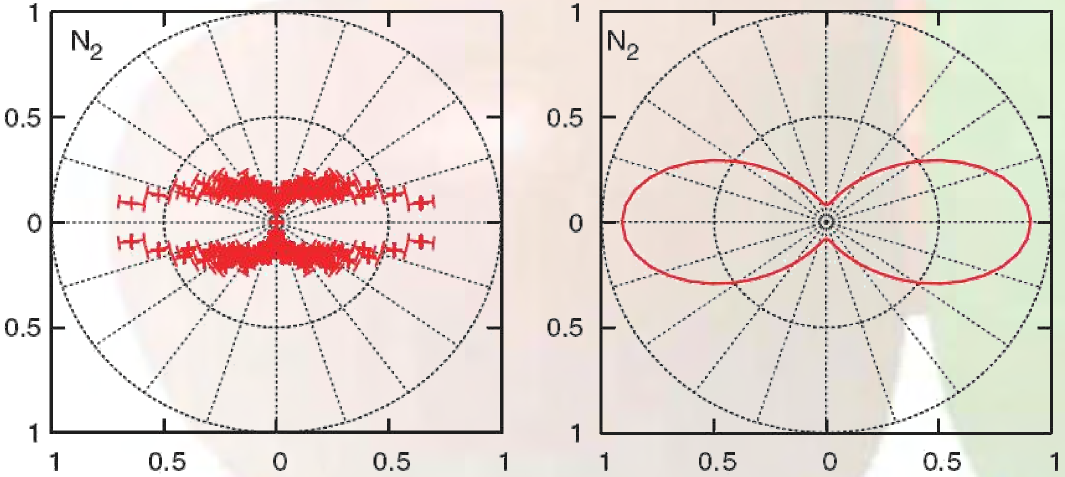
Motivation

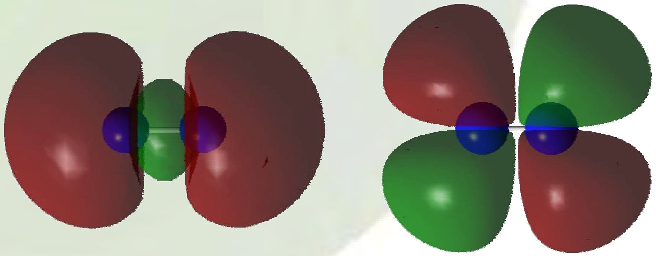
- Ionization + dissociation of molecules in linearly polarized laser fields
- Ionization rates depend on the orientation and alignment of molecules, they are correlated to the elecron density of HOMO
- Long pulses cause post-ionization alignment, which distorts the picture



Schematic of the ionization process



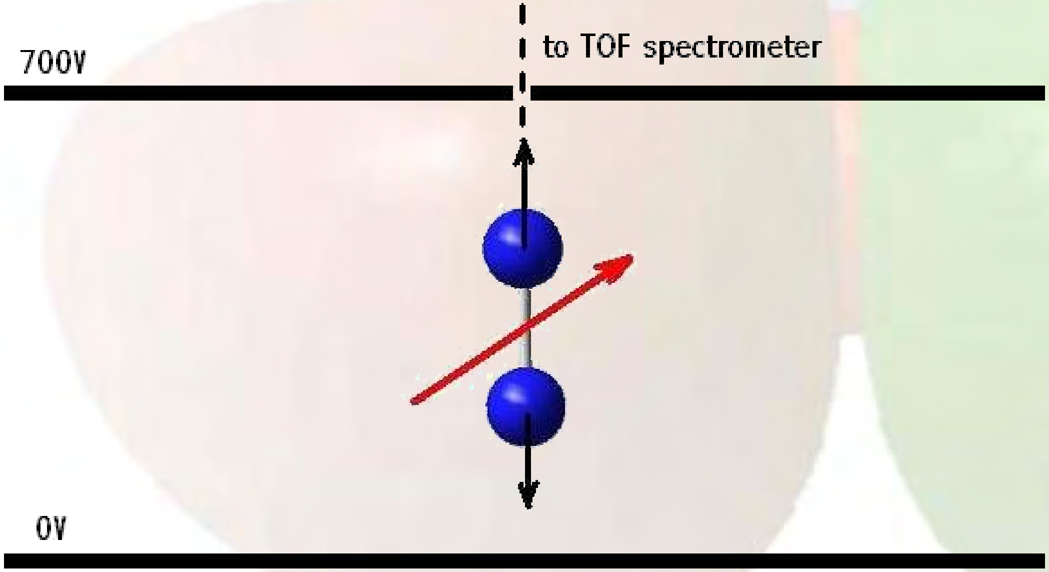
Observed and calculated angular distribution of fragmentation of N_2 molecule

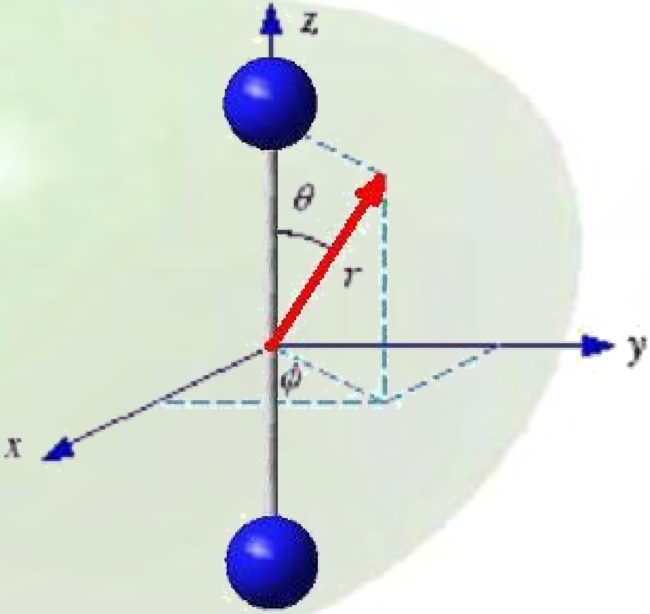


HOMO and LUMO of N2

Experiment

- Molecules in a chamber are exposed to a fast laser pulse, focused under a small opening
- They undergo dissociative ionization, and are accelerated by electric field
- Only the dissociative fragments aligned with the TOF axis are detected



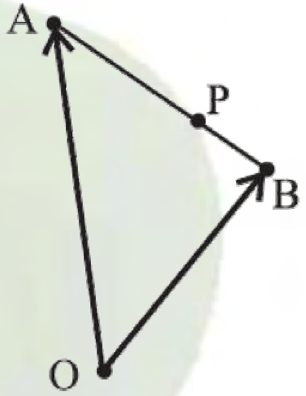


Gaussian Functions

- Linear Combination of Atomic Orbitals: $\psi_i = \sum_{\mu=1}^{n} c_{\mu i}\phi_\mu$
- Stater type orbitals (STOs): $r^{n-1}e^{-\xi r/a_0}Y_l^m$.
- Gaussian primitives: $g(\alpha, l, m, n; x, y, z) = Ne^{-\alpha r^2}x^l y^m z^n$

  -possible to separate integrals for different degrees of freedom

  -Gaussian product theorem – speedup of 4-5 orders of magnitude compared to STO



$$P_M(x,y,z)e^{-\alpha(\mathbf{r}-\mathbf{R_A})^2}Q_N(x,y,z)e^{-\beta(\mathbf{r}-\mathbf{R_A})^2}$$
$$= R_{M+N}(x,y,z)e^{-(\alpha+\beta)(\mathbf{r}-\mathbf{R_P})^2}$$

$$\mathbf{R_P} = \frac{\alpha\mathbf{R_A} + \beta\mathbf{R_B}}{\alpha+\beta}$$

R_{M+N} is polynomial in *M+N*

- Basis functions are linear combinations of Gaussian primitives; exponents and coefficients in combination are derived from atomic HF calculations

Basis Sets

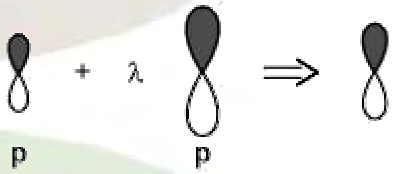
- Minimal basis set STO-nG: a set number of basis functions for every atomic orbital of each free atom, but with the same exponent for all subshells within the same n

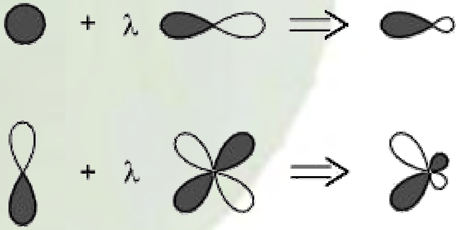
- Split valence basis set X-YZG:

  core 1s orbital is a sum of X gaussian primitives,

  Valence shells 2s and 2p are split into:

  - Inner part: sum of Y gaussian primitives
  - Outer, more difuse part is sum of Z gaussian primitives
  - And so on…





- X-YZG* Adding polarisation functions to account for the distortion of the orbitals caused by the other nuclei

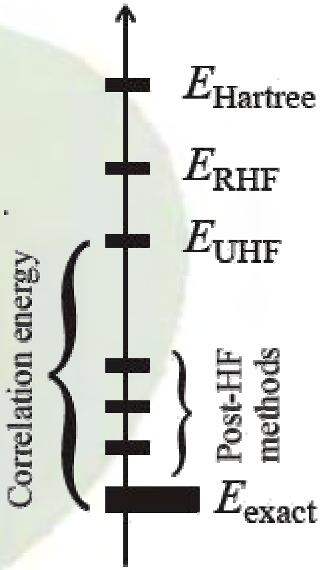
- X-YZ+G Adding diffuse functions

Theory

- Born-Oppenheimer approximation: $\hat{H} = \cancel{\hat{T}_N(\mathbf{R})} + \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r},\mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$

  constant, added at the end of calculation

- Theory levels:
  - Hartree Fock – self consistent solution of $E_{\mathrm{HF}} = \langle \Psi_{\mathrm{HF}} | \hat{H} | \Psi_{\mathrm{HF}} \rangle \geq E$ for one electron at a time, in an average field generated by the other nuclei; does not account for correlation energy
  - MP2 – many body perturbation theory of the second order
  - QCISD(T) – introduced by expanding the phase space to include unoccupied orbitals $\Psi = c_0 \Psi_{\mathrm{HF}} + \sum_{i}^{\mathrm{occ}} \sum_{r}^{\mathrm{vir}} a_i^r \Psi_i^r + \sum_{i<j}^{\mathrm{occ}} \sum_{r<s}^{\mathrm{vir}} a_{ij}^{rs} \Psi_{ij}^{rs} + \cdots$ the coefficients are then obtained variationally
  - CC – coupled cluster, describes corellation in terms of interacting clusters of electrons

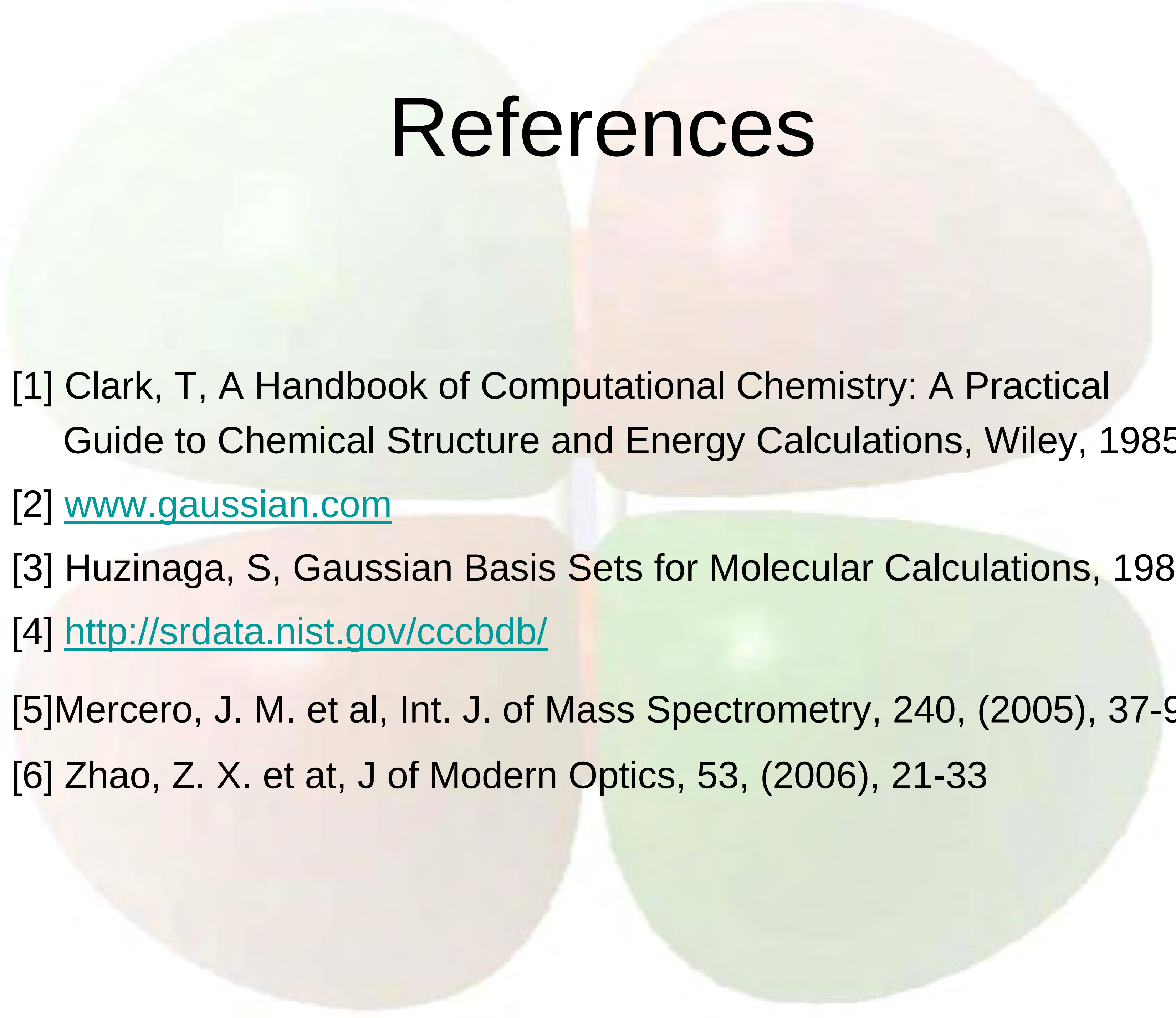


Results - summary

- Calculations for N_2 molecule, using Gaussian 3.09
- Basis sets used: 3-21G, 6-31G, 6-31+G(d), 6-311G, 6-311+G(d)
- Calculations failed to predict the correct form of HOMO

Theory	Bond length error	Vibr. Fr error	Ion. Pot. error	Effects on accuracy when increasing the basis
HF	1-3%	10-15%	~1%	Accuracy decreases
MP2	1-4%	8-25%	6-22%	
CI	0.5-3%	--	1-7%	Increases, esp. when adding polarization functions
CC	0.5-3%	--	1-7%	

References



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