ICPEAC Tutorial

45 Years of Computational Atomic and Molecular Physics: What Have We (I) Learned

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July 25, 2017

The Equations for Atoms and Molecules

$$\mathbf{H}(\mathbf{r};\mathbf{R})|\Psi> = E|\Psi>$$

$$\mathbf{H}(\mathbf{r};\mathbf{R}) = \sum_i \mathbf{T_i} + \sum_{i,q} \mathbf{V_{i,q}} + \sum_{i<j} \mathbf{V_{i,j}} + \sum_i \mathbf{U_i(t)}$$

$$\left[i\frac{\partial}{\partial t} - \mathbf{H}(\mathbf{r},t;\mathbf{R})\right]|\Psi>$$

$$\mathbf{T_i} = -\frac{1}{2}\nabla_i^2, \quad \mathbf{V_{i,q}} = -\frac{Z}{|\mathbf{r_i} - \mathbf{R_q}|}, \quad \mathbf{V_{i,j}} = \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}, \quad \mathbf{U_i}(t) = \mathbf{E}(t)\cdot\mathbf{r_i}$$

The Unreasonable Effectiveness of Mathematics in the Natural Sciences

The miracle of the appropriateness of the language of mathematics for the formulation of the laws of physics is a wonderful gift which we neither understand nor deserve. We should be grateful for it and hope that it will remain valid in future research and that it will extend, for better or for worse, to our pleasure, even though perhaps also to our bafflement, to wide branches of learning.

Eugene Wigner 1960

Ok, but how do we go beyond this to uncover new or previously overlooked physics ?

Motivation

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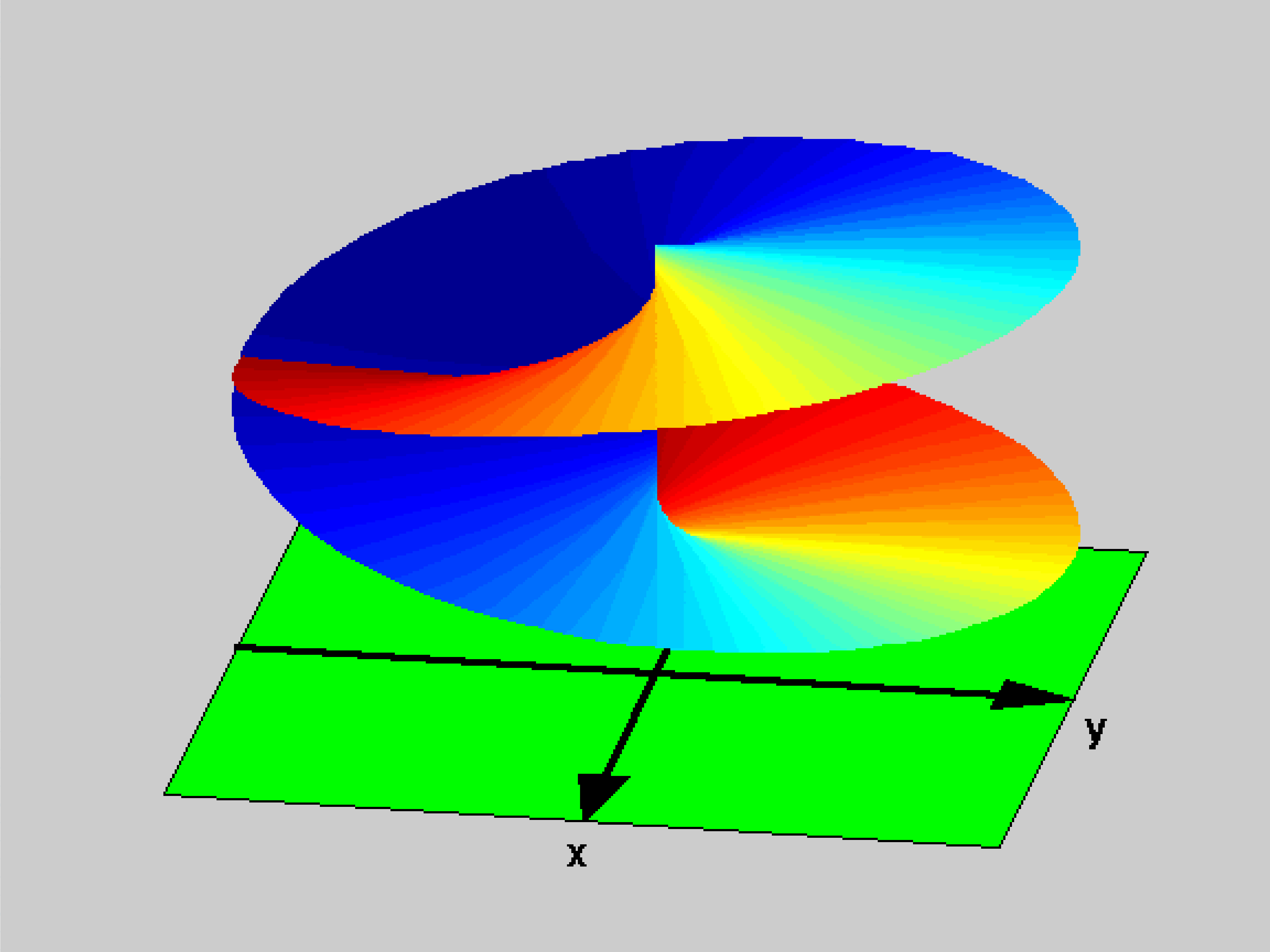


Sqrt(z)

Focus

- Progress in treating Scattering and Resonances in the Time Independent Schrödinger Equation – Shape & Feshbach
  - Stabilization and Complex scaling – For resonances and more(?)
  - Equvalent quadrature
  - R-Matrix and J-Matrix Method(s)
  - Complex-Kohn Method

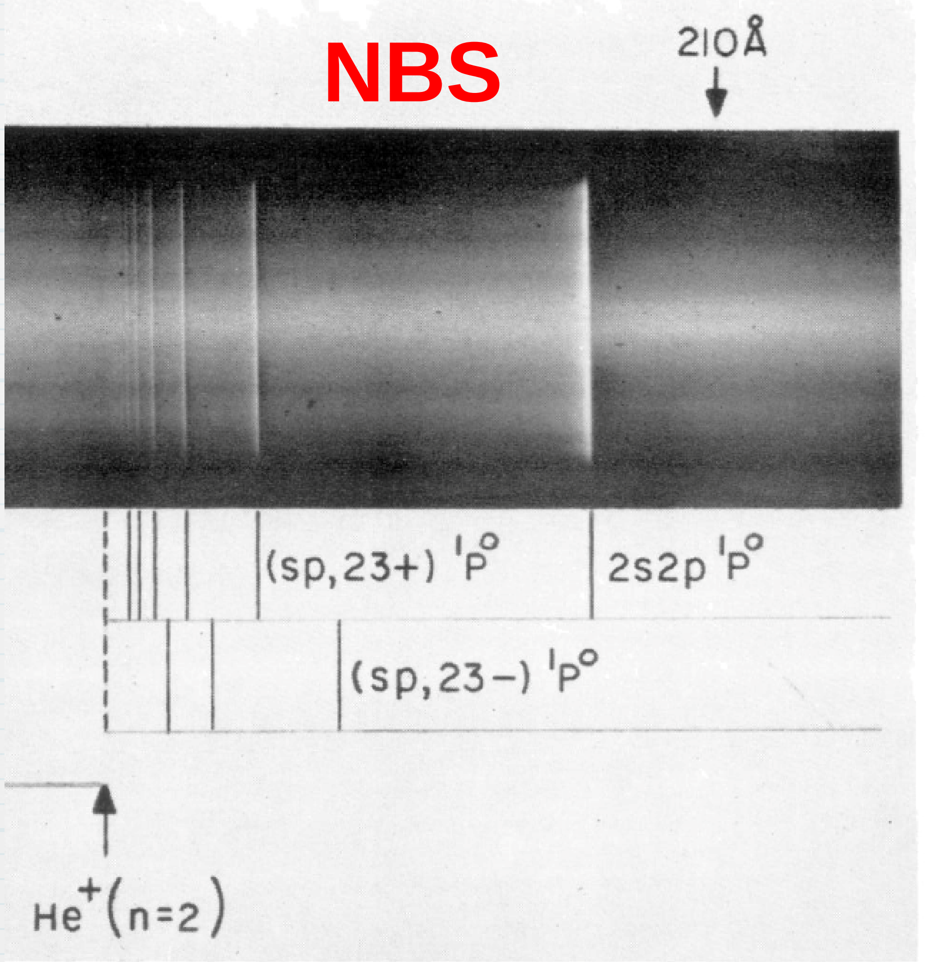
⇓

- Progress in treating the Time Dependent Schrödinger Equation in ultrashort (10^{-18} sec), intense EM Fields – Making electrons dance

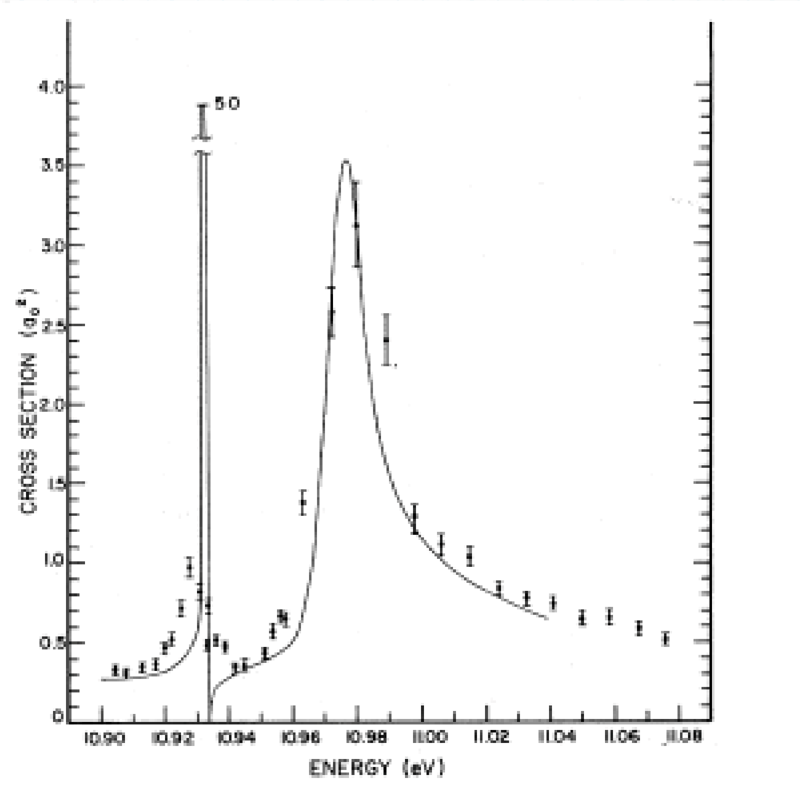
  - Propagation of the TDSE by CI

The Phenomena: Photoabsorbtion

Discovered at NBS



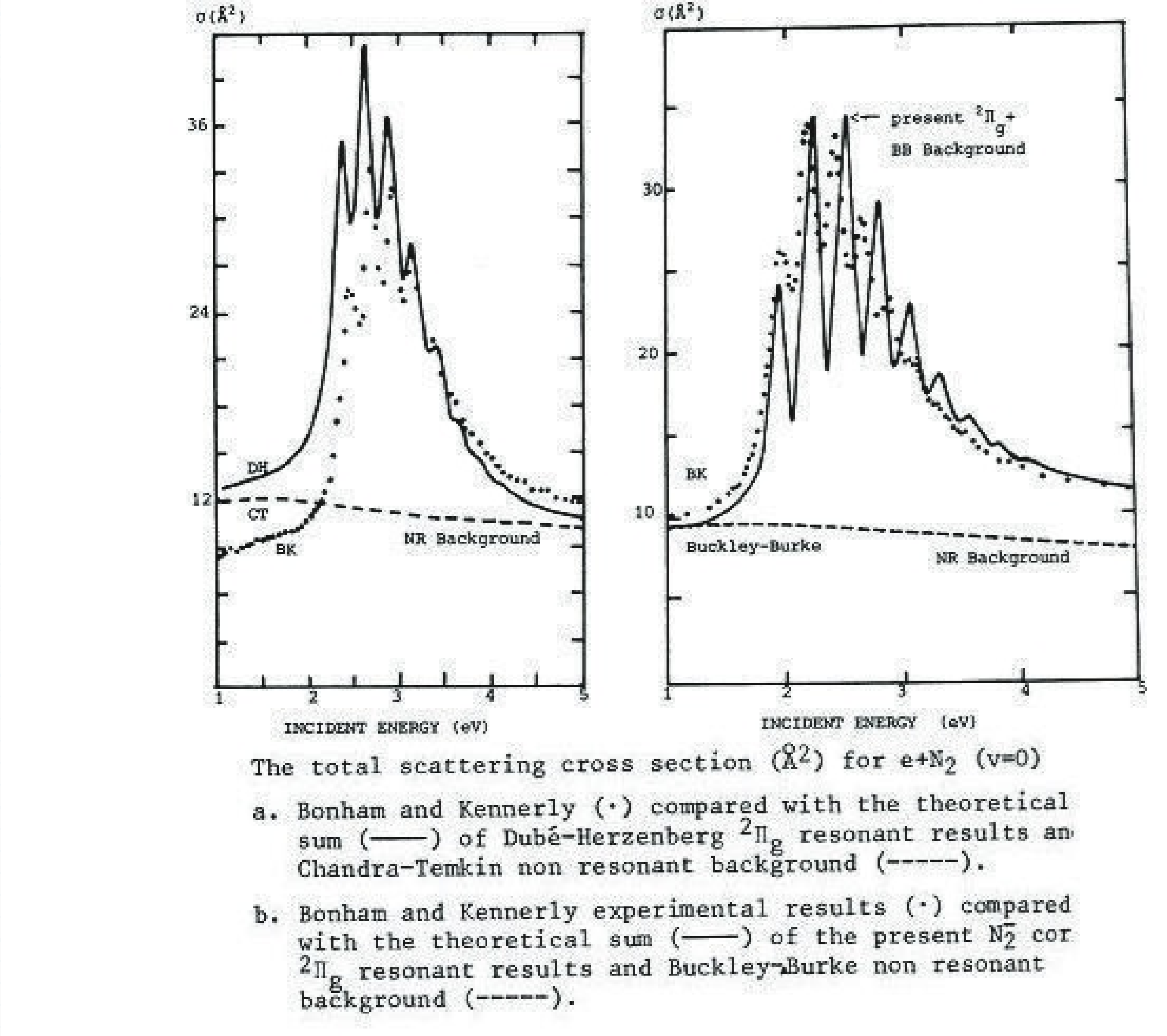
H^-



Note the sharp lines appearing in a continuous spectum

What are they??

The Phenomena:Electron Scattering



The total scattering cross section (Å^2) for e+N_2 (v=0)

a. Bonham and Kennerly (·) compared with the theoretical sum (——) of Dubé-Herzenberg $^2\Pi_g$ resonant results an Chandra-Temkin non resonant background (-----).

b. Bonham and Kennerly experimental results (·) compared with the theoretical sum (——) of the present N_2 cor $^2\Pi_g$ resonant results and Buckley-Burke non resonant background (-----).

Note the peaks appearing in a scattering cross section

What are they??

The Early Days

- Use standard scattering methods
  - ➢ Solve coupled 1D equations – extract phase shifts

Difficult for atoms – Very difficult for molecules

- People (mostly chemists) begin to think.

  Hmm, Can we *cheat* ? - modify bound state methods (or otherwise) to treat scattering processes.

  Carefully taking continuum limit

$$i\epsilon \rightarrow 0$$

  - ➢ A computational experiment: Expansions in L^2 functions approximate scattering functions to within a normalization
  - ➢ How to extract information – Stabilization (Taylor) – Equivalent quadrature (Heller, Yamani, Reinhardt), Complex rotation (Reinhardt, McCurdy, Rescigno, etc.) - Still alive and well after 45 years

The Early Days

Stabilization – Howard Taylor

Early observation: For resonances the energy "stabilizes" with the size of the L^2 basis set. Phase shifts can be extracted at the eigenvalues (Frank Harris, Bob Nesbet)

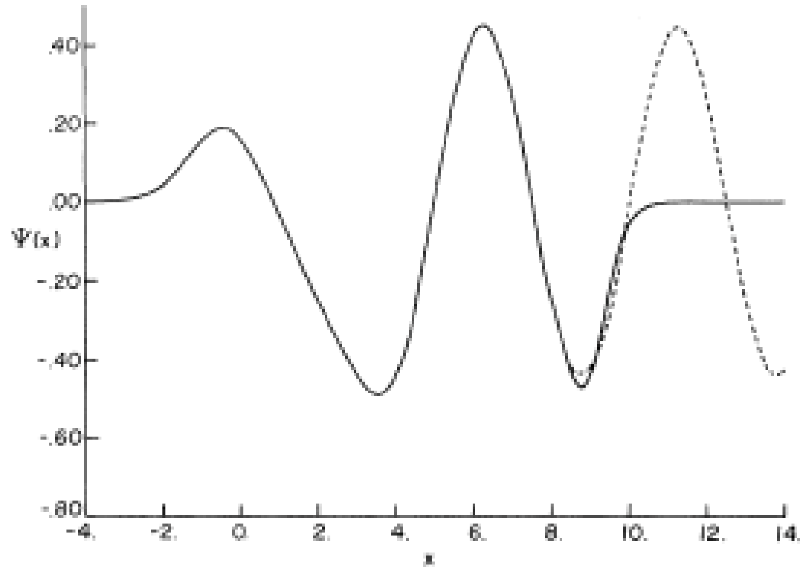
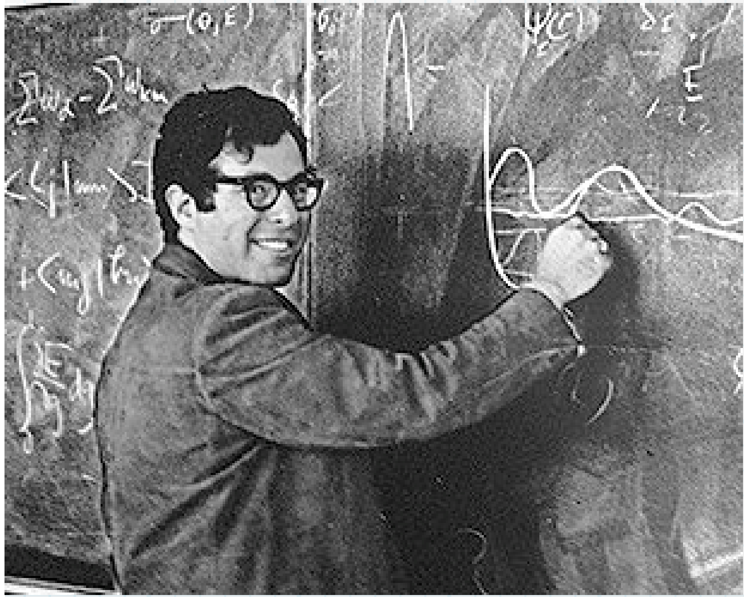


FIG. 4. Comparison of the exact and approximate wave functions in the nonresonant region for $\lambda = 0.225$. (solid line) Φ_j^N with $N = 50$, $j = 4$, and $\epsilon_j^N = 0.788675$; (dashed line) Ψ_E for $E = \epsilon_j^N$.



pproach

of

Howard S. Taylor

9/17/1935 – 4/17/2015

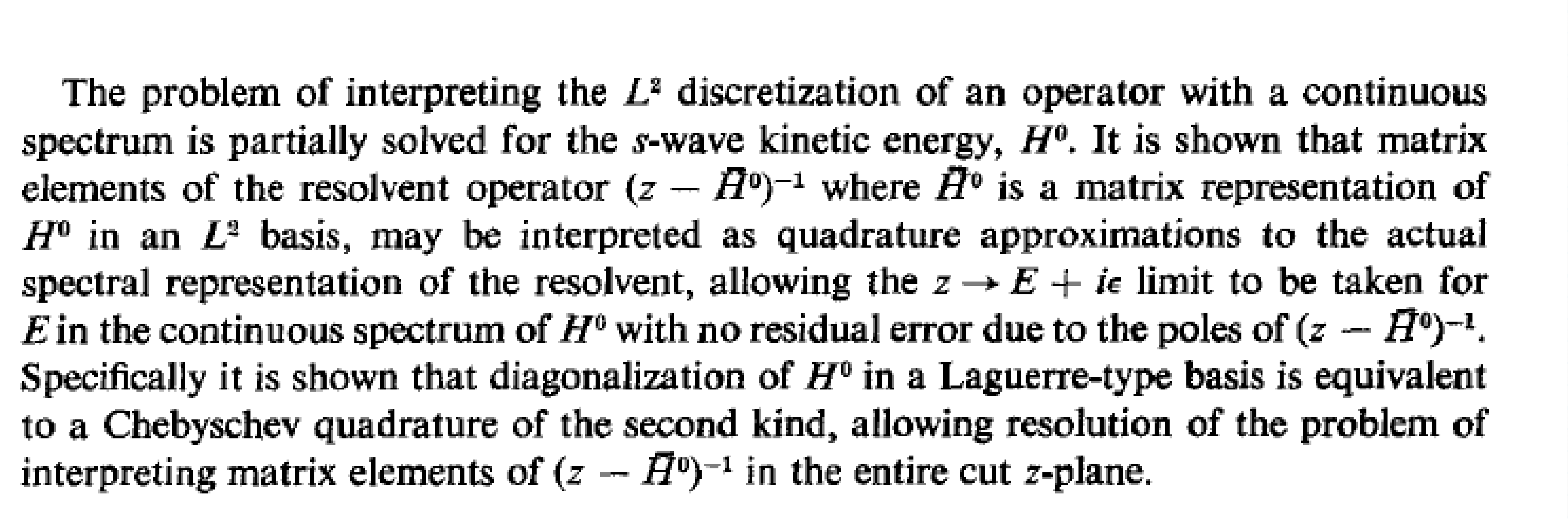
Complex Rotation – An Odd Idea?

$$r \to r\exp(i\theta)$$

- **Originally used to compute only resonance positions and widths - Barry Simon – Resonances rotated into lower half of complex plane and exposed – decaying basis can be used - BUT**
- **Scaling the inner orbitals gave numerical problems – They decayed but oscillated wildly [** $\exp[-\alpha r\exp(i\theta)]$ **]**
- **The non-analyticity of the electron-nuclear interaction make it impractical to scale just the electronic coordinate in the BO approximation**
- **Can be reformulated to use complex exponents – More robust**
- **Sharp or smooth exterior complex scaling – Rotate outside a radius r=R. Produces only outgoing waves and scattering information can be extracted.**

The Early Days

Equivalent Quadrature



The problem of interpreting the L^2 discretization of an operator with a continuous spectrum is partially solved for the s-wave kinetic energy, H^0. It is shown that matrix elements of the resolvent operator $(z - \bar{H}^0)^{-1}$ where $\bar{H}^0$ is a matrix representation of H^0 in an L^2 basis, may be interpreted as quadrature approximations to the actual spectral representation of the resolvent, allowing the $z \to E + i\epsilon$ limit to be taken for E in the continuous spectrum of H^0 with no residual error due to the poles of $(z - \bar{H}^0)^{-1}$. Specifically it is shown that diagonalization of H^0 in a Laguerre-type basis is equivalent to a Chebyschev quadrature of the second kind, allowing resolution of the problem of interpreting matrix elements of $(z - \bar{H}^0)^{-1}$ in the entire cut z-plane.

$$\langle f \,|\, (E + i\epsilon - H^0)^{-1} \,|\, f\rangle$$

$$\approx \sum_{i=1}^{N} \frac{\omega_i \,|\langle f \,|\, E_i\rangle|^2}{E_0 - E_i} + |\langle f \,|\, E_0\rangle|^2 \left\{ \int_0^{E^{\max}} \frac{dE}{E_0 - E} - \frac{\omega_i}{E_0 - E_i} \right\} - i\pi \,|\langle f \,|\, E_0\rangle|^2$$

$$|\langle f \,|\, E_i^0\rangle|^2 \equiv |\langle f \,|\, \chi_i\rangle|^2 / \omega_i^{\mathrm{Eq}}$$

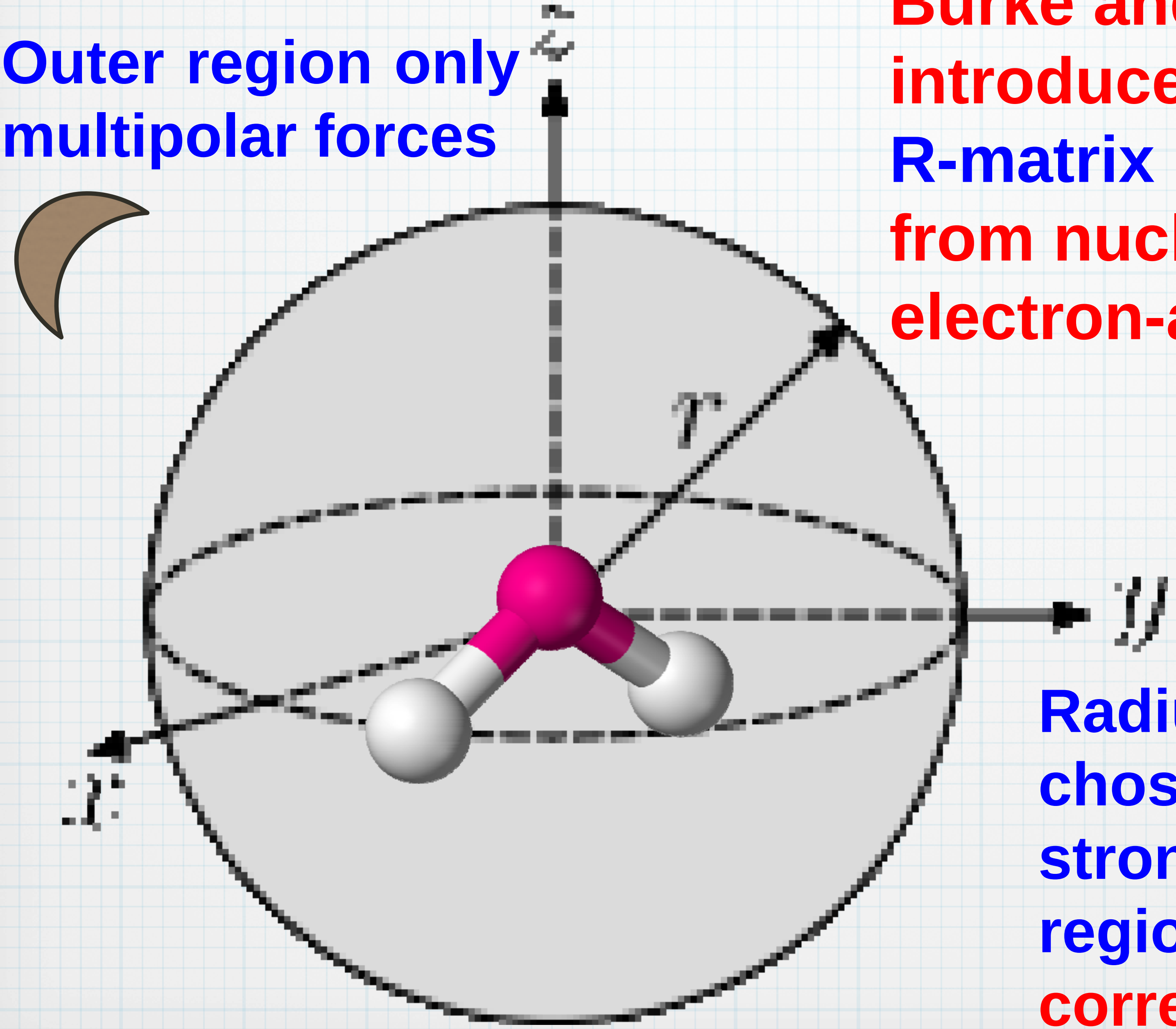
Normalization difference gives weights.

What Did We Learn

- Bound state techniques, suitably modified, can be used to extract scattering information.
- The original methods provided insight, but perhaps with the exception of ECS were clumsy.
- The real complications of scattering boundary conditions need only be faced at long range where the physics becomes simpler.

So, how can we effectively combine bound state methods at short range with other techniques at long-range to extract scattering information

An Important Concurrent Development



Outer region only multipolar forces

Burke and co-workers introduce a computational R-matrix idea borrowed from nuclear physics into electron-atom scattering.

Radius of sphere chosen to enclose strong interaction region – exchange, correlation

R-Matrix Method

$$H_{N+1}(\mathbf{r};\mathbf{R})\Psi^{\Gamma}(\mathbf{r};\mathbf{R}) = E(\mathbf{R})\Psi^{\Gamma}(\mathbf{r};\mathbf{R})$$

Anticipate molecules

$$L_{N+1} = \sum_{i=1}^{N+1} \frac{1}{2}\delta(r_i - a)\left(\frac{\partial}{\partial r_i} - b\right)$$

$$\Big[H_{N+1}(\mathbf{r};\mathbf{R}) + L_{N+1} - E(\mathbf{R})\Big]\Psi^{\Gamma}(\mathbf{r};\mathbf{R}) = L_{N+1}\Psi^{\Gamma}(\mathbf{r};\mathbf{R})$$

$$\Big[H_{N+1}(\mathbf{r};\mathbf{R}) + L_{N+1} - E_i(\mathbf{R})\Big]\Psi_i^{\Gamma}(\mathbf{r};\mathbf{R}) = 0$$

- Just like any other bound state eigenvalue problem. Solve by diagonalization at each R to get potential curves for the (N+1) electron system

- Bloch Operator to ensure Hermiticity
- Basis functions satisfy fixed logarithmic derivative on surface of sphere – slow convergence, not easy for molecules
- Schneider and others realize no need for fixed BC – use any basis set – BO assures Hermiticity and accelerates convergence – enabled molecular calculations

The Full Theory - Mind Your P's and Q's

- The total wavefunction is divided into a P-space and Q-space part.
- P-space carries asymptotic information about possible breakup channels
- Q-space describes correlation and other shorter range phenomena

P-space – explict channel ennumeration

$$\psi_{c,i}^{\Gamma} = \mathcal{A}[\Phi_c^{\Gamma}(\mathbf{X}_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}; \mathbf{R}) u_{c,i}^{0}(r_{N+1})]$$

$$\Phi_c^{\Gamma}(\mathbf{X}_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}; \mathbf{R}) = \Phi_c^{SM_S}(\mathbf{X}_N, \sigma_{N+1}; \mathbf{R}) Y_{\ell_c m_{\ell_c}}(\theta_{N+1}, \phi_{N+1})$$

$$\Phi_c^{SM_S}(\mathbf{X}_N, \sigma_{N+1}; \mathbf{R}) = \sum_{M_{S_c} m_c} \Phi_c(\mathbf{X}_N; \mathbf{R}) \chi_{\frac{1}{2} m_c}(\sigma_{N+1}) (S_c M_{S_c} \frac{1}{2} m_c | S M_S)$$

Q-space $\chi_q^{\Gamma}(\mathbf{X}_{N+1}; \mathbf{R})$

The Scattering Wavefunction

$$\Psi^{\Gamma} = \sum_k \frac{\Psi_k^{\Gamma}}{[E_k(\mathbf{R}) - E(\mathbf{R})]} < \Psi_k^{\Gamma} | L_{N+1} | \Psi^{\Gamma} >$$

Projecting this onto channel states, setting the radial variable to its value at the R-Matrix surface, gives

$$y_c(a_0) = \sum_{d=1}^{n} \mathcal{R}_{c,d} [\frac{\partial u_d(r)}{\partial r} - b u_d(r)]|_{r=a_0}$$

(Hope) connections to quantum defect theory will be made in the last tutorial

$$\mathcal{R}_{c,d} = \frac{1}{2} \sum_k \frac{u_{c,k}(a_0) u_{d,k}(a_0)}{[E_k(\mathbf{R}) - E(\mathbf{R})]}$$

Matching provides Scattering information

$$u_{c,k}(a_0) = \sum_i a_{c,i,k} u^0_{c,i}(a_0)$$

Some Remarks

- For practical reasons, for polyatomics, the basis sets must be Gaussians
- As a consequence of the finite box, the tails of integrals involving diffuse Gaussians need to be subtracted - in practice not a problem - use multipole expansions
- As we showed, a single diagonalization provides the information to extract the full scattering K-matrix for all E. Thus any resonances are readily found without the need for complex rotation, complex basis functions or any non-hermitian mathematics.
- Treatment of the external region depends on the nature of the problem but it is crucial that only local potentials are important outside the R-matrix box. Often simply matching to free waves is sufficient
- Internal and external dynamics dominated by different Physics – Can be exploited

J-Matrix Method

- Expand in special L^2 basis that;
  - Represents both solutions to the “free” particle Hamiltonian asymptotically
  - Leads to a three term recursion relationship which is exactly soluble for the free particle
  - Expand potential in finite subset of the “complete” basis at short range.
  - Asymptotic solutions are known “exactly” in the basis

❖ Leads to a tridiagonal matrix problem that can be solved for the scattering information

❖ Can be viewed as an R-matrix like method

Direct connections to equivalent quadrature but in function not real space.

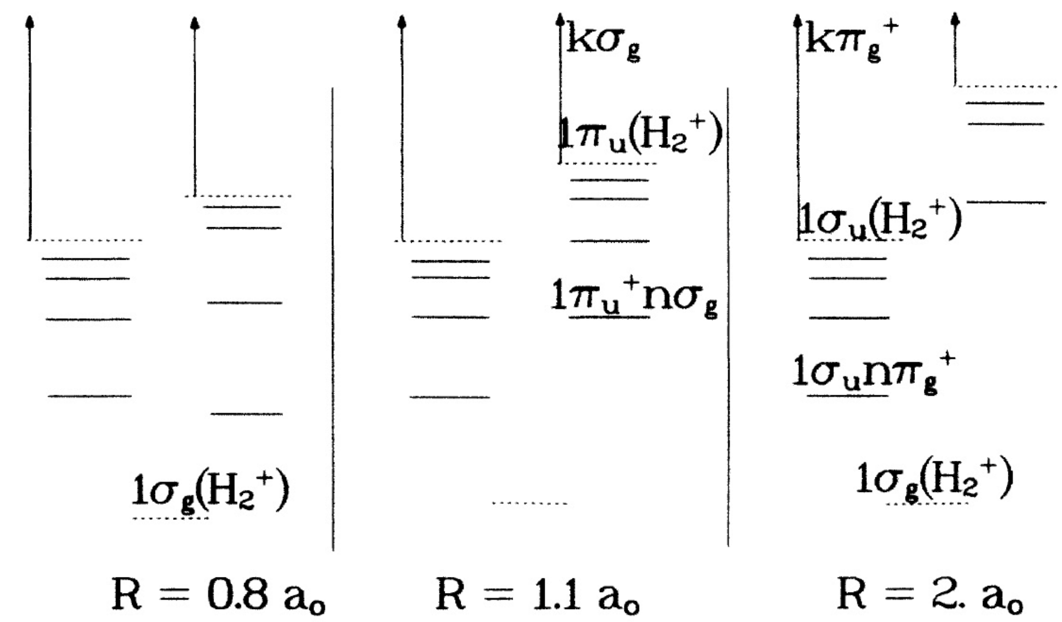
What Happens When the Nuclei Move ?

- **Adiabatic Nuclei Approximation**- Take scattering amplitudes computed at fixed geometry, multiply by a ro-vibrational wavefunction and integrate over nuclear coordinates to produce;

$$f_{d\nu_d j_d m_{j_d}, c\nu_c j_c m_{j_c}}(\mathbf{k}\cdot\hat{\mathbf{r}}) = \langle \chi_{\nu_d}(R) Y_{j_d, m_{j_d}}(\hat{\mathbf{R}}) | f_{dc}(\theta', \phi') | \chi_{\nu_c}(R) Y_{j_c m_{j_c}}(\hat{\mathbf{R}}) \rangle$$

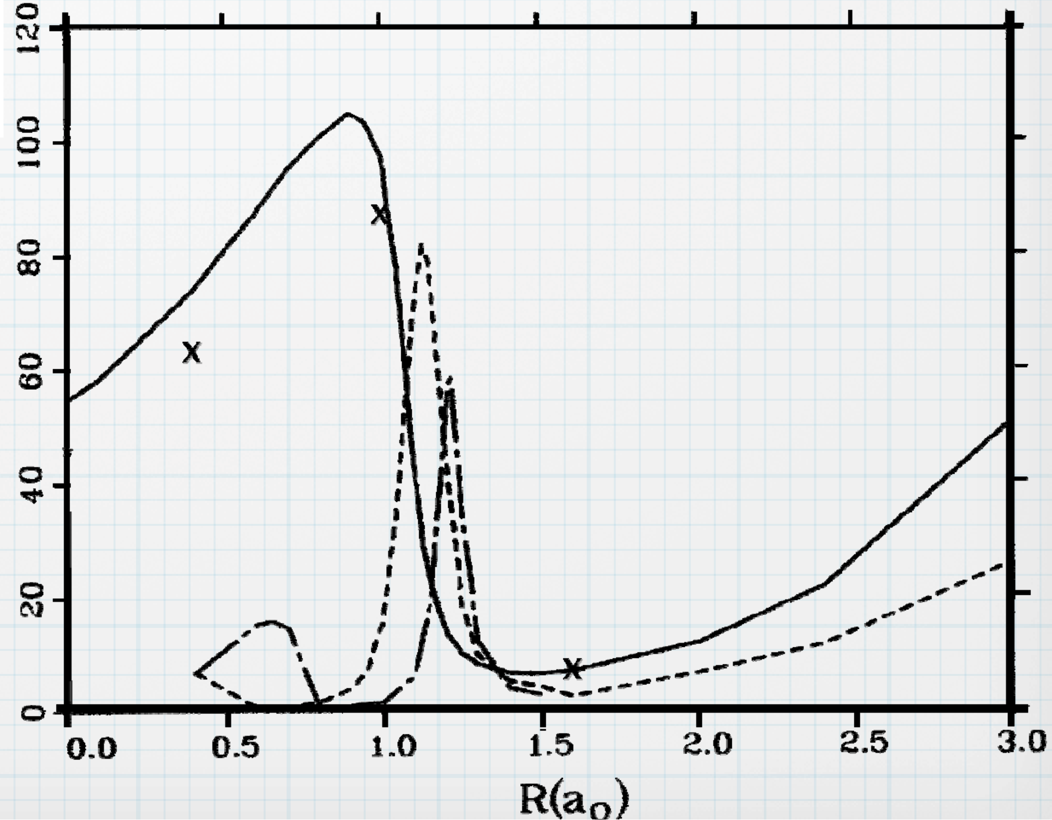
  - Works when electron collision times are short compared to nuclear motion
  - Fails to describe threshold effects(energetics certainly and possibly dynamics)
  - Fails to describe many resonance phenomena

Dueling Resonances in H_2: A Computational Discovery with Fixed Nuclei

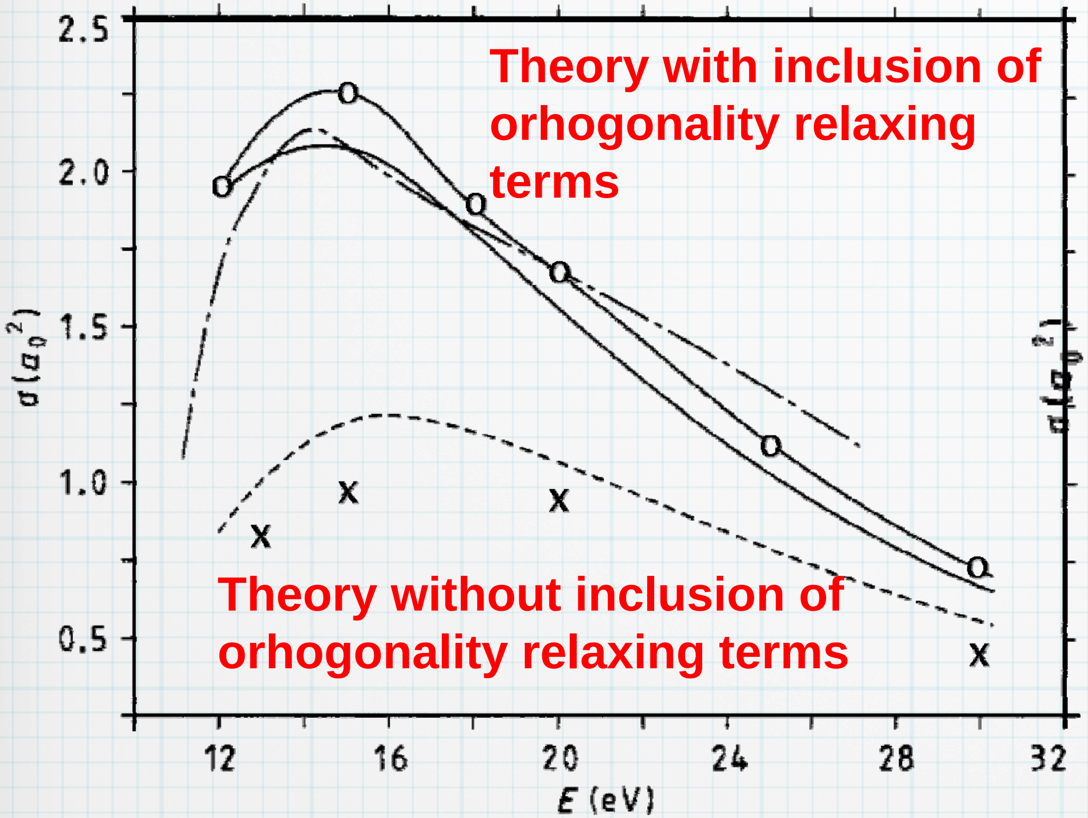


Doubly excited state level structure of $^1\Pi_u$ symmetry with R

Behavior of lowest resonance with R. Note changes in width due to curve crossing

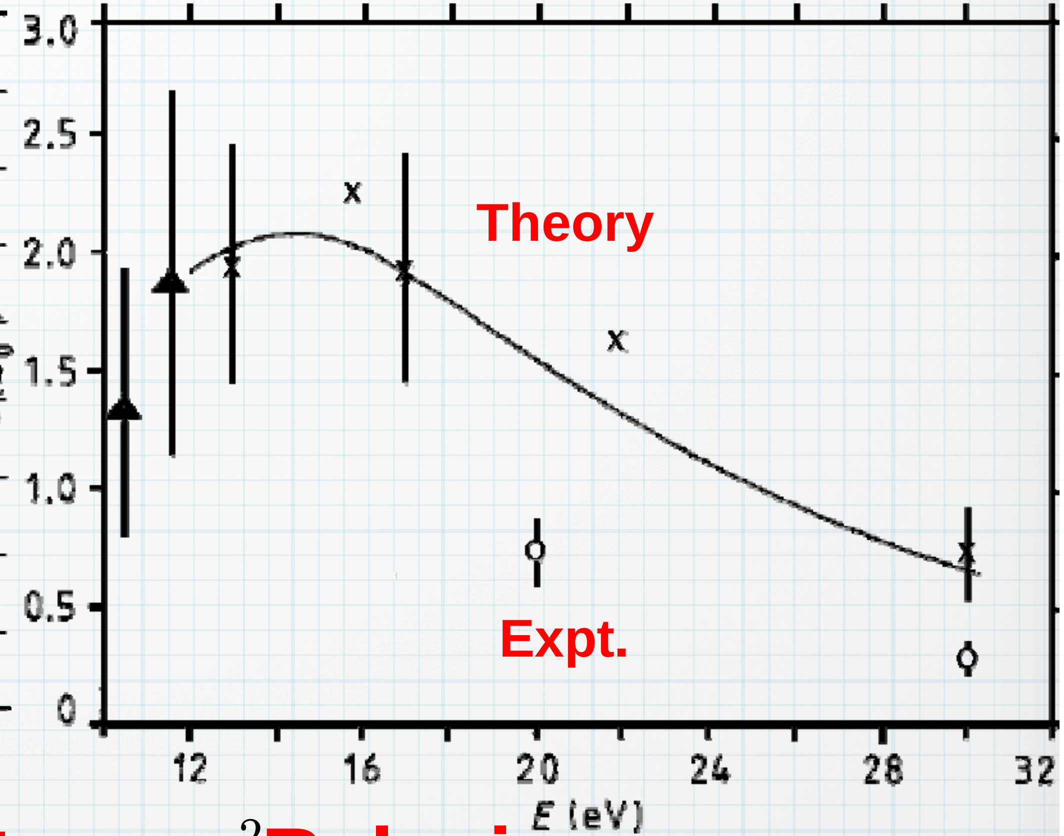


Two State Close Coupling in e + H_2: Importance of Orthogonality



Theory with inclusion of orhogonality relaxing terms

Theory without inclusion of orhogonality relaxing terms



Theory

Expt.

Excitation of ground to $b^3\Sigma_u$: Relaxing orthogonality constraints via CC or Optical Potential

Note: Even today disagreement between best CCC and earlier results

What Happens When the Nuclei Move ?

- **Beyond Adiabatic Nuclei Approximation** - Is it necessary to completely couple the electronic and nuclear degrees of freedom non-adiabatically everywhere ?
  - Can a local BO treatment at short range be relaxed at long range to produce sensible results.
  - Is the key to the answer contained in the idea of the R-matrix.
  - How can this be integrated into the formalism and computational scheme.

Full Electronic plus Nuclear SE

$$\Psi^{\Gamma}(\mathbf{X}_{N+1};R) = \sum_{k} \Psi_k^{\Gamma}(\mathbf{X}_{N+1};R)\Theta_k^{\Gamma}(R)$$

$$\left[H_{N+1} + L_{N+1} + L_R - E\right]\Psi^{\Gamma} = \left[L_{N+1} + L_R\right]\Psi^{\Gamma}$$

$$\begin{aligned}\left[T_R + L_R + E_k(R) - E\right]\Theta_k^{\Gamma}(R) &= \left(\Psi_k^{\Gamma} \mid L_{N+1} + L_R \mid \Psi^{\Gamma}\right) \\ &= \frac{1}{2}\sum_{c\nu_c} u_{c,k}(a_0,R)\chi_{\nu_c}(R)\left[\frac{\partial}{dr} - b\right]u_{c,\nu_c}(r)\mid_{r=a_0} \\ &+ \frac{1}{2\mu}\sum_{[AB]_i} u_{[AB]_i,k}(R)\delta(R-A_0)\left[\frac{\partial}{dR} - B_0\right]u_{[AB]_i}(R)\end{aligned}$$

Vibr. excitation

Dissociation

The Spectral R-Matrix and its Physical Interpretation

$$\mathcal{R}_{c\nu_c,d\nu_d} = \frac{1}{2}\sum_{k,q}\left\langle \chi_{\nu_c}(R) \mid u_{c,k}(a_0,R) \mid \theta_{k,q}(R)\right\rangle \left[\epsilon_{k,q}-E\right]^{-1}\left\langle \theta_{k,q}(R') \mid u_{d,k}(a_0,R') \mid \chi_{\nu_d}(R')\right\rangle$$

$$\mathcal{R}_{c\nu_c,i} = \frac{1}{2\mu}\sum_{k,q}\left\langle \chi_{\nu_c}(R) \mid u_{c,k}(a_0,R) \mid \theta_{k,q}(R)\right\rangle \left\langle \theta_{k,q}(A_0) \mid \left[\epsilon_{k,q}-E\right]^{-1} \mid u_{[AB]_i,k}(A_0)\right)$$

$$\mathcal{R}_{i,c\nu_c} = \frac{1}{2}\sum_{k} u_{[AB]_i,k}(A_0) \mid \theta_{k,q}(A_0)\right\rangle \left[\epsilon_{k,q}-E\right]^{-1}\left\langle \theta_{k,q}(R) \mid u_{c,k}(a,R) \mid \chi_{\nu_c}(R)\right\rangle$$

$$\mathcal{R}_{i,j} = \frac{1}{2\mu}\sum u_{[AB]_i,k}(R_0) \mid \theta_{k,q}(A_0)\right\rangle \left[\epsilon_{k,q}-E\right]^{-1}\left\langle \theta_{k,q}(A_0) \mid u_{[AB]_j,k}(A_0)\right)$$

Simple Interpretation

- **If numerator varies slowly with R – Factor to get Franck-Condon Overlaps between N and (N+1) Electron Vibrational states**
- **Denominators vanish at compound state vibrational energies**

Step 1
Get the curves

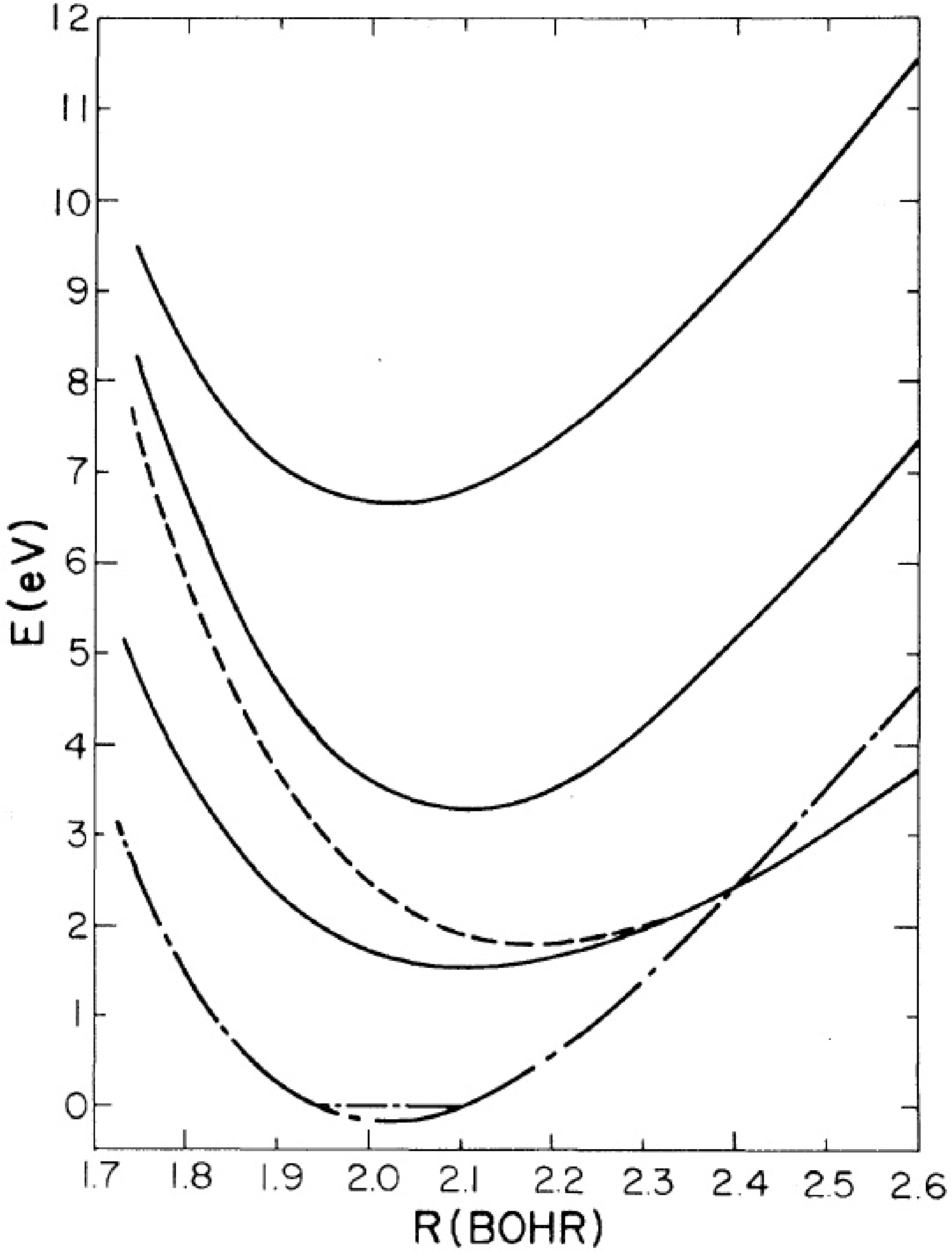
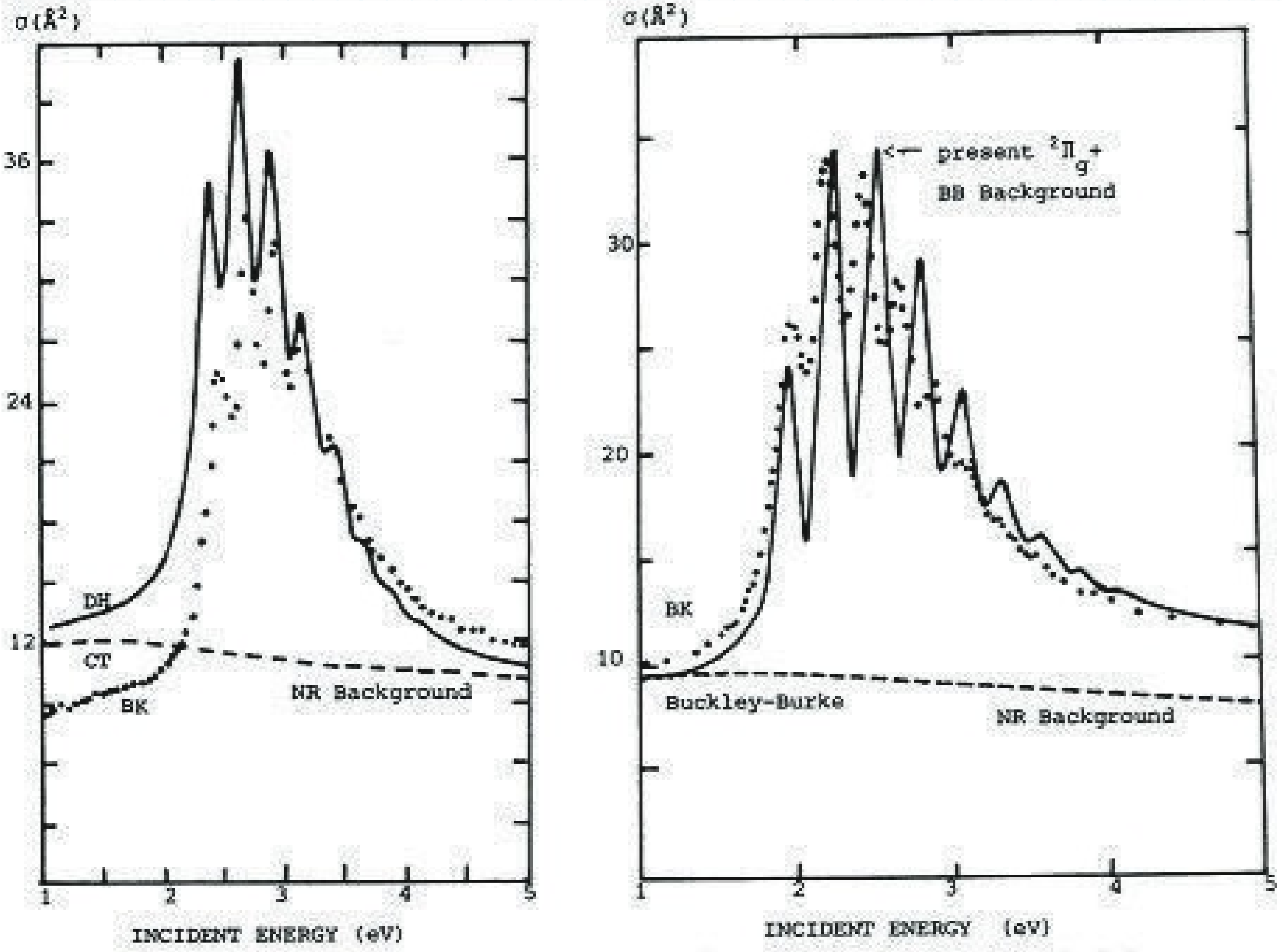


FIG. 1. Potential curves for N_2 and N_2^-: dash-dotted line, ground state of N_2; dotted line, resonant state of N_2^-; and solid line, *R*-matrix states of N_2^-.

These were computed at the SCF level for the negative ion just as HST would have done

Two-particle-one-hole calculations give equivalent results

The Proof of the Pudding



The total scattering cross section (Å^2) for e+N_2 (v=0)

a. Bonham and Kennerly (·) compared with the theoretical sum (——) of Dubé-Herzenberg $^2\Pi_g$ resonant results an Chandra-Temkin non resonant background (-----).

b. Bonham and Kennerly experimental results (·) compared with the theoretical sum (——) of the present N_2^- cor $^2\Pi_g$ resonant results and Buckley-Burke non resonant background (-----).

More Pudding:Comparison with Vibrational CC

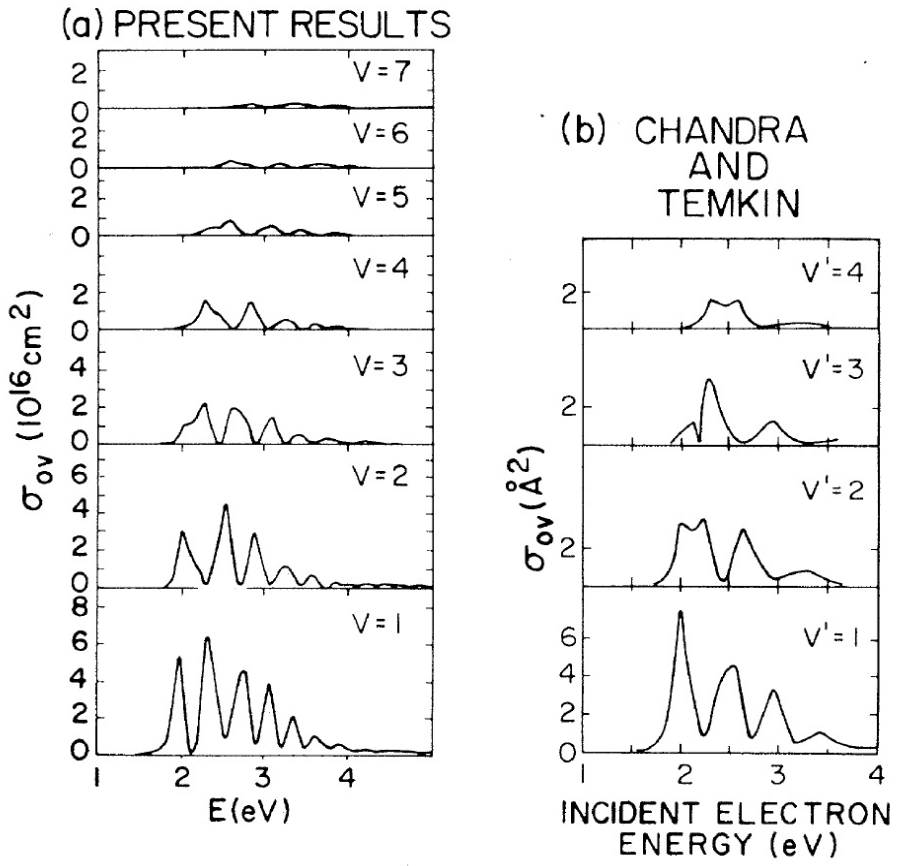
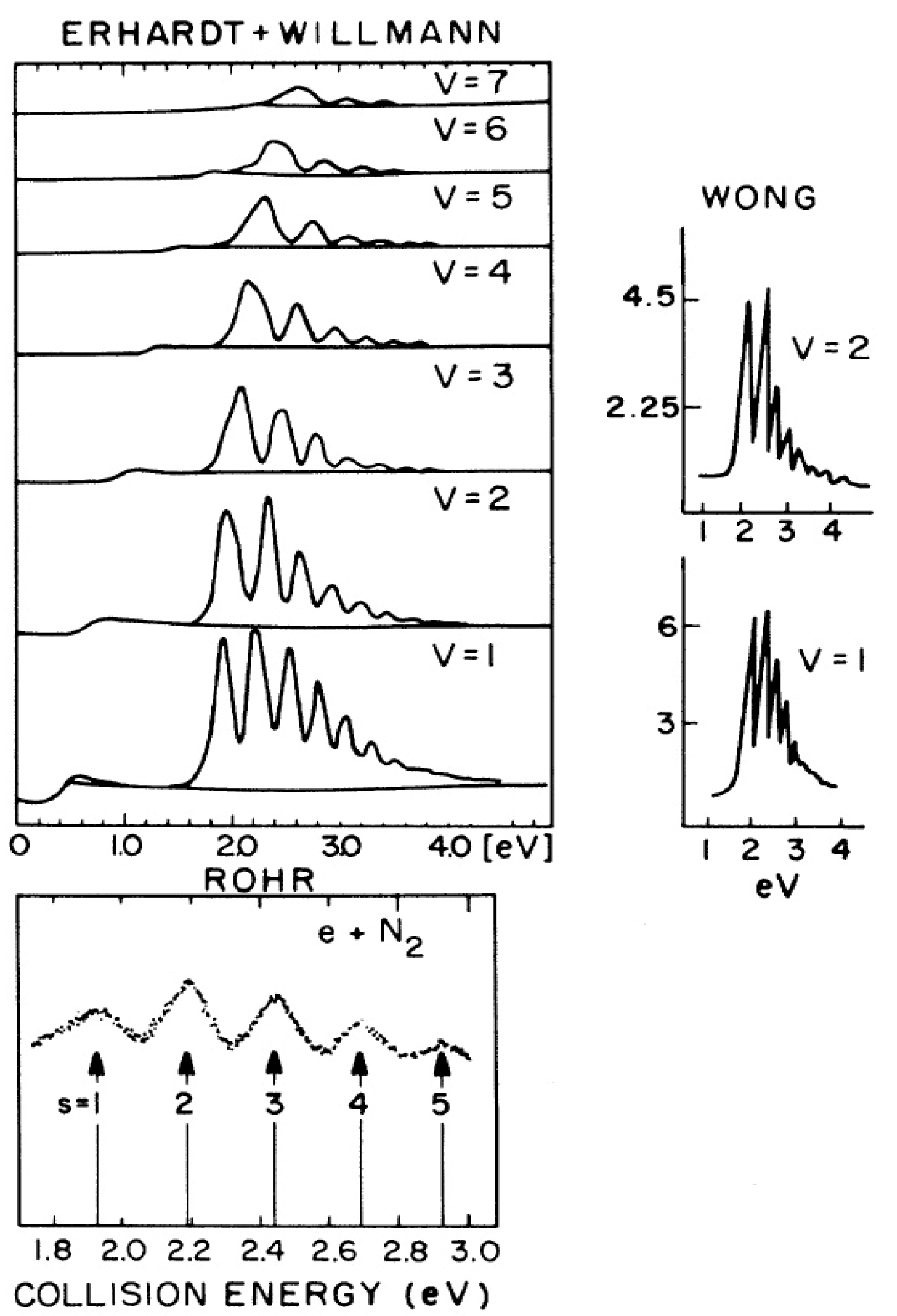


FIG. 4. Comparison of calculated cross sections for vibrational excitation in N_2.



Our theoretical results nailed the open question of the normalization of the X-section

Summary of R-Matrix Contributions

- The R-matrix idea of separating regions dominated by different physical effects can give rise to important conceptual and computational simplifications
- BO s ge – Can
  be e hniques
  to co ered by
  HST
- Elec d if
  nece n positive
  ions.

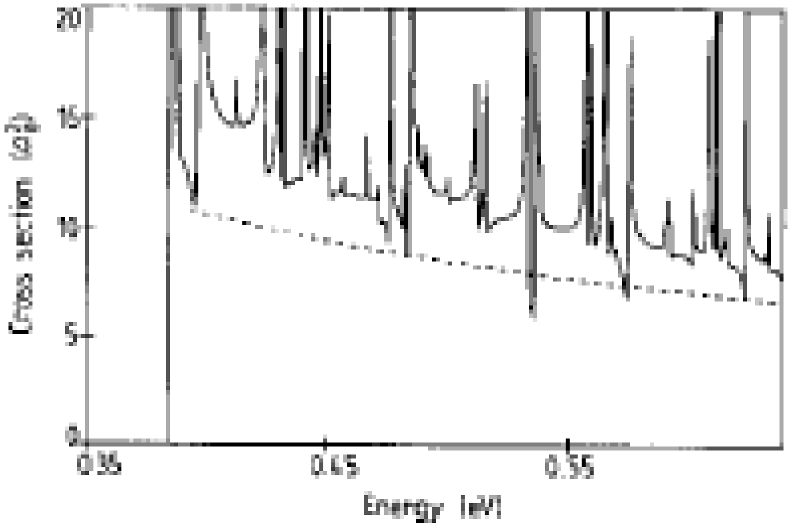


Figure 6. Total non-adiabatic $v = 0 \rightarrow 1$ cross section; the broken curve shows the total adiabatic cross section of figure 4.

HeH –Tennyson
Curve X-ing is
important

- Transform wavefunction at molecular core to include rovibrational effects WHEN NEEDED.

Concurrent Development Complex Kohn Method

The variational principle

$$|\Psi^{\Gamma}> = \sum_{\Gamma'} |\Phi_{\Gamma'} F^{\Gamma}_{\Gamma'}> + \sum_{\mu} d^{\Gamma}_{\mu} |\Theta_{\mu}>$$

$$[T^{\Gamma}_{\Gamma'}] = T^{\Gamma}_{\Gamma'} - 2 < \Psi_{\Gamma} | H - E | \Psi_{\Gamma'} >$$

Expand

$$|F^{\Gamma}_{\Gamma'}> = \sum_{\Gamma'} [f^{\Gamma}_{\Gamma'} \delta_{\Gamma\Gamma'} + T^{\Gamma}_{\Gamma'} g^{\Gamma}_{\Gamma'}] + \sum_{q} c^{\Gamma}_{\Gamma' q} \psi_q$$

The coefficients are found by varying the stationary expression with respect to the parameters to get the trial T

$\Theta_\mu =$ a L^2 $\mathbf{N+1}$wavefunction $\quad \psi_q =$ a L^2 one-electron orbital

$f^{\Gamma'}_{\Gamma}(r) =$ a regular radial function such as a spherical Bessel or Coulomb function

$g^{\Gamma'}_{\Gamma}(r) =$ an irregular radial function such as a spherical Neumann or Coulomb function regularized at the origin

Properties of Complex Kohn Method

- One electron orbitals MUST span the “internal” region
- One electron continuum functions are orthogonalized to **ALL** one electron bound orbitals.
- No spurious poles in T-matrix due to using Hankel function as outgoing wave – **complex symmetric matrix**
- All direct coulomb-like integrals done analytically when Gaussian basis sets employed – **Important for molecular scattering**
- Using separable expansions the non-coulomb integrals between Gaussian and continuum

Optical Potential Formalism

$$Q = \sum_{\mu} |\Theta_{\mu} >< \Theta_{\mu}|$$

$$P = I - Q$$

$$H_{eff} = H_{PP} + (H - E)_{PQ}(E - H)_{QQ}(H - E)_{QP}$$

Variation of the parameters leads to algebraic equations which when solved and substituted back into the variational expression, yields,

$$[\mathbf{T}] = -2\big(\mathbf{M}_{00} - \mathbf{M}_{0q}\mathbf{M}_{qq}^{-1}\mathbf{M}_{q0}\big)$$

The matrix elements are defined only into the space spanned by the spherical incoming and outgoing waves and q

The matrix Mqq may be computed using standard L^2 methods of quantum chemistry

Polyatomic Scattering using the CKM

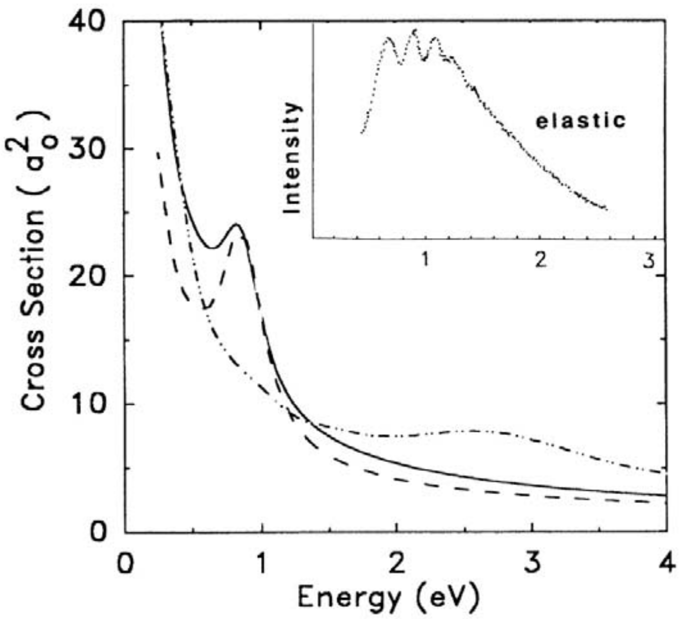


FIG. 1. Elastic differential cross section for e^--CH_2O. Solid curve: optical-potential results at 90°; dashed curve: optical-potential results at 120°; dash-dotted curve: static-exchange result at 90°. Inset: Experimental results of Benoit and Abouaf (Ref. 8).

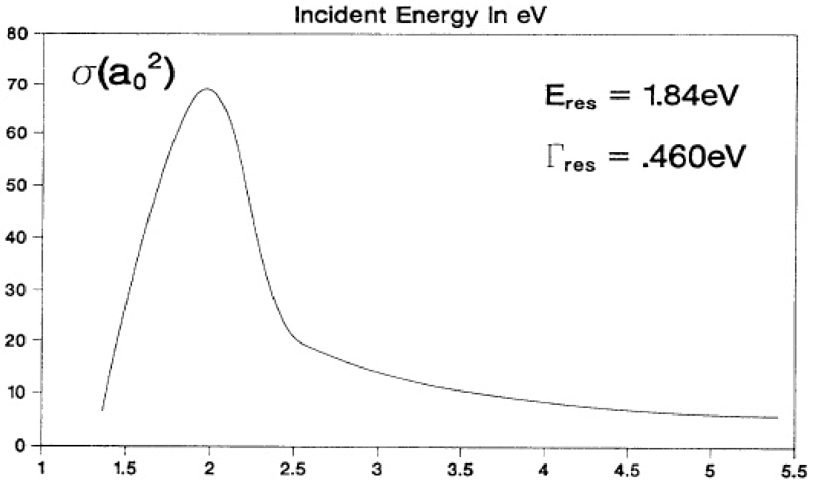


FIG. 1. $^2B_{2g}$ partial integrated cross section for e^--C_2H_4 scattering.

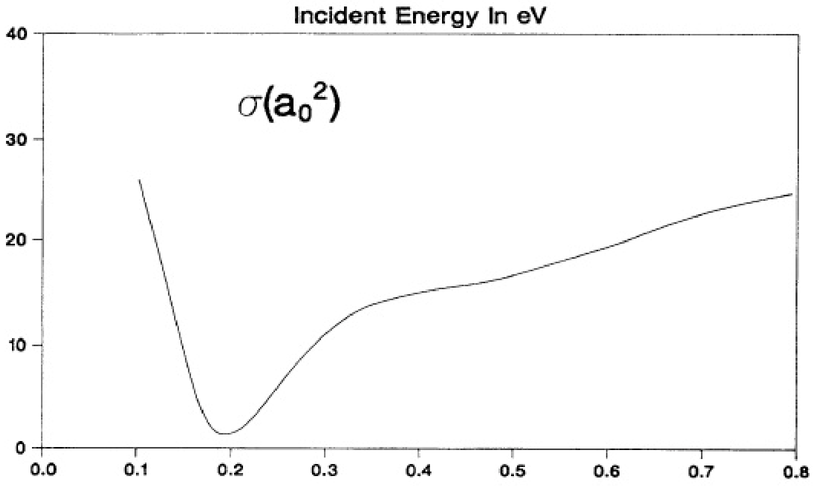
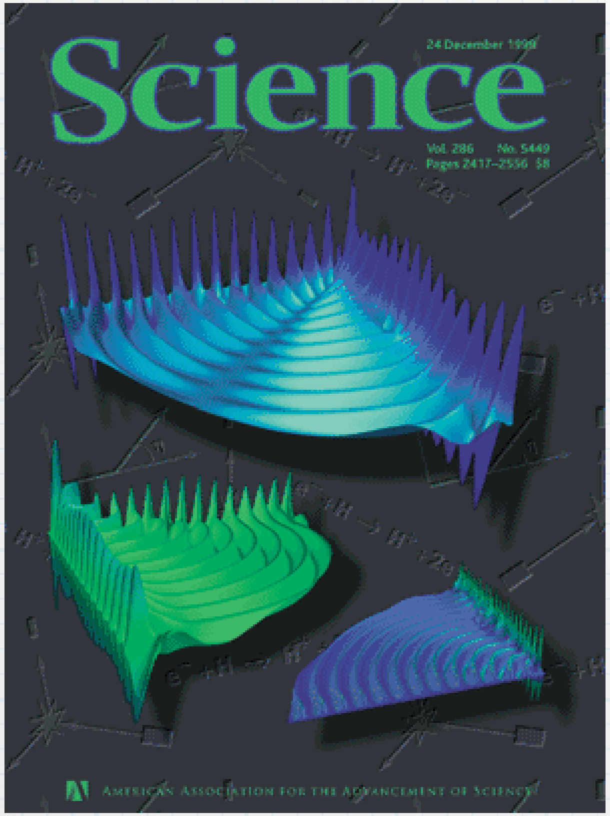


FIG. 2. ^2A_g partial integrated cross section for e^--C_2H_4 scattering.

What about Impact Ionization

- All methods discussed so far do not treat three particle breakup – impact ionization
- Three Coulomb particles – no analytic solution known for all E and all angles

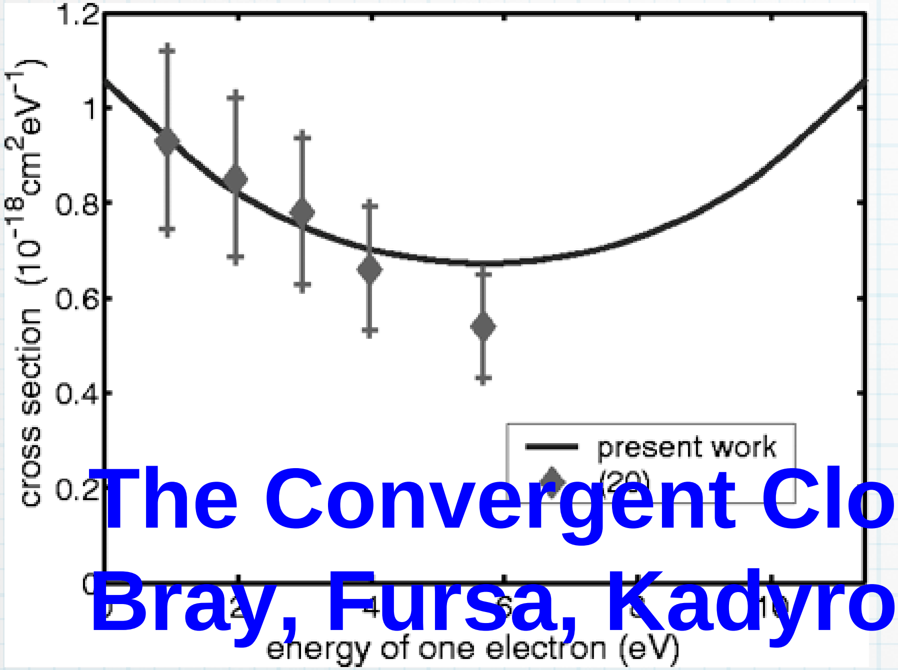


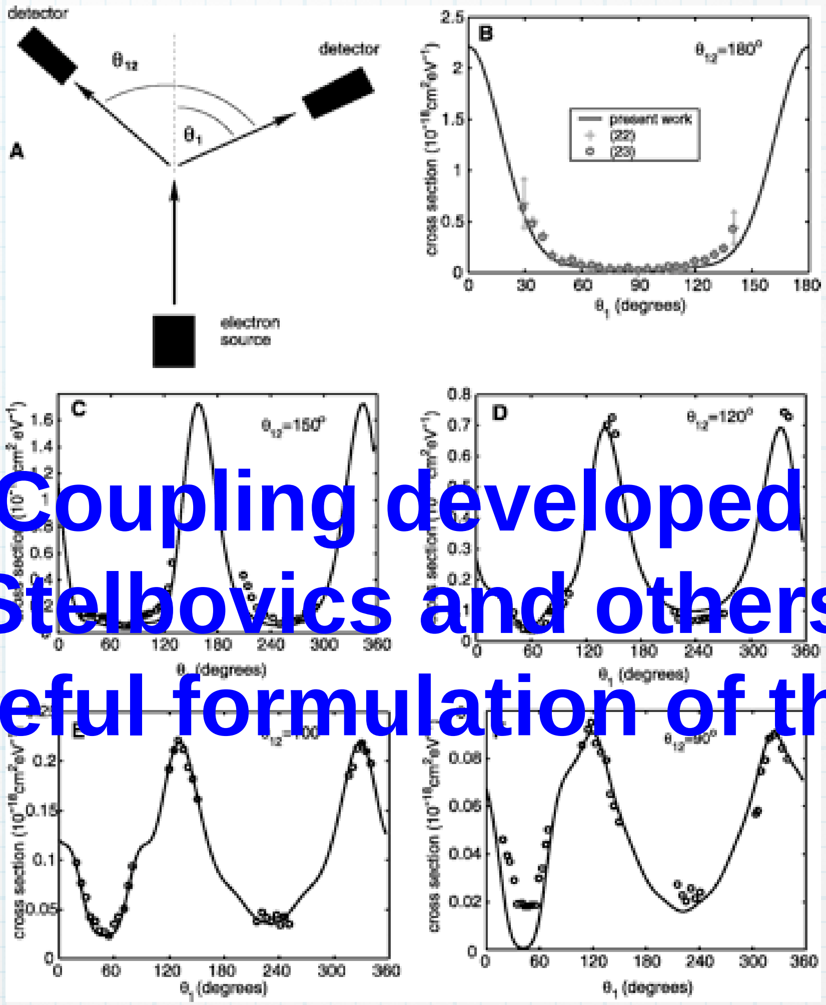
An electron colliding with a hydrogen atom to yield two electrons and a proton is the simplest example of electron-impact ionization. Mathematically formulated in the 1950s, this three-body problem in quantum mechanics has required supercomputers for its solution. Shown are wave functions for the breakup of a system of three charged particles. Understanding collisional ionization is essential for problems such as low-temperature plasma formation.

How was this problem solved

- **Wavefunction expanded in partial waves**
- **Coupled PDE's in the radial coordinate discretized using FD**
- **The key- ECS to *directly* avoid scattering BC's- Price paid is a large ($5x10^6$) set of sparse, complex, algebraic equations – not particularly well conditioned**
- **Scattering information extracted using flux – better approaches using integral formula developed later**

Some Results





The Convergent Close Coupling developed by Bray, Fursa, Kadyrov, Stelbovics and others offers an alternative useful formulation of the problem.

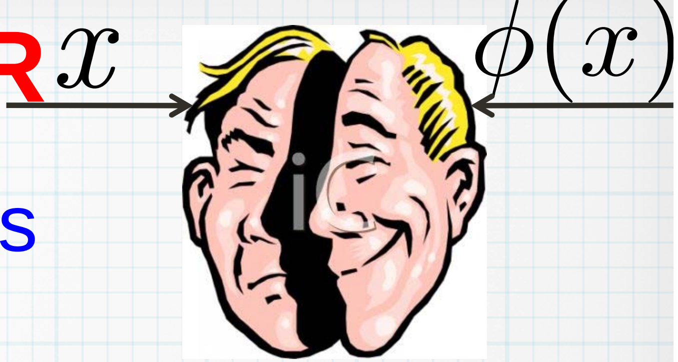
Single differential ionization cross section (SDCS) for electron-hydrogen collisions at 25-eV incident energy. At E/2 = 5.7 eV there is equal energy sharing, as expected.

Geometrical arrangement for the equal energy-sharing, coplanar, triple differential cross sections (TDCSs) shown. The two detectors are tuned to measure electrons with half of the total energy.

The Time Dependent Approach

- **Work with wavepackets having an energy spread in collisions problems or fixed initial state in photon collisions**
- **Important to take limits carefully**
- **Advantage that there is no need to impose boundary conditions – analyze the wavefunction by projection at large distances**
- **Propagation in time may need to be carried out for large distances and long times to compute experimental observables – Other approaches such as ECS can avoid this.**

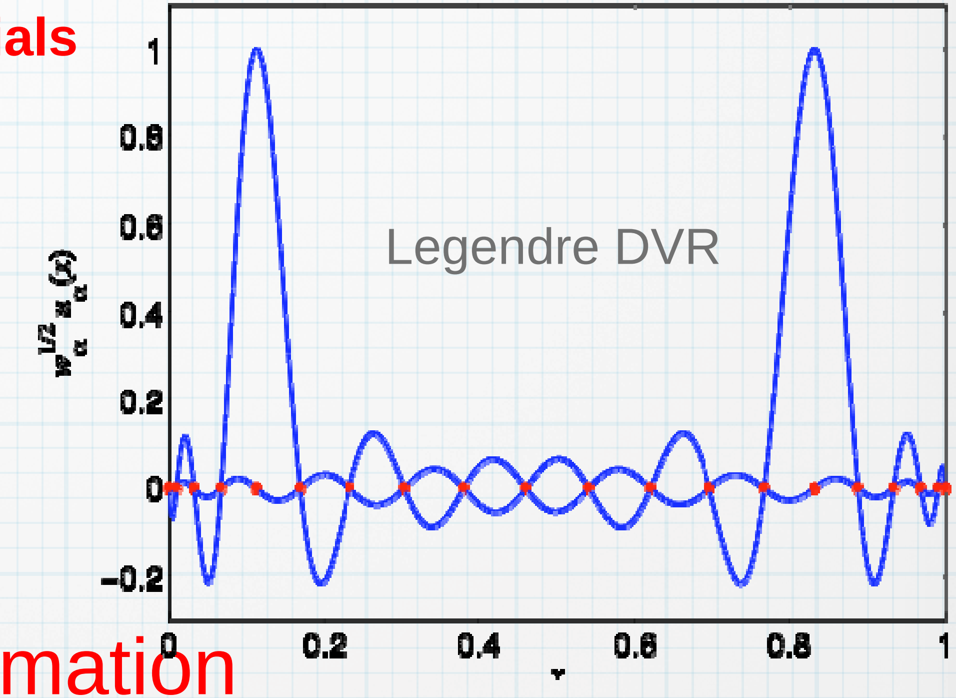
A New Sort of Basis: The DVR



Define a set of “coordinate” functions

$$u_i(x) = w_i \sum_{n=1}^{N} \phi_n(x)\phi_n(x_i)$$

Orthogonal Polynomials



with the property

$$u_i(x_j) = \delta_{i,j}$$

and

$$< u_i|x|u_j >= \delta_{i,j} x_i$$

The DVR makes the approximation that;

$$< u_i|F(x)|u_j >= \delta_{i,j} F(x_i)$$

This has been shown to be accurate provided the basis (quadrature) is large enough.

DVR are actually Lagrange interpolating polynomials normalized on the integration mesh

The Finite Element DVR Basis

Properties

* Each coordinate divided into elements of arbitrary size

* Each element has an arbitrary number of DVR functions but the objective is to use the minimal number for the accuracy required

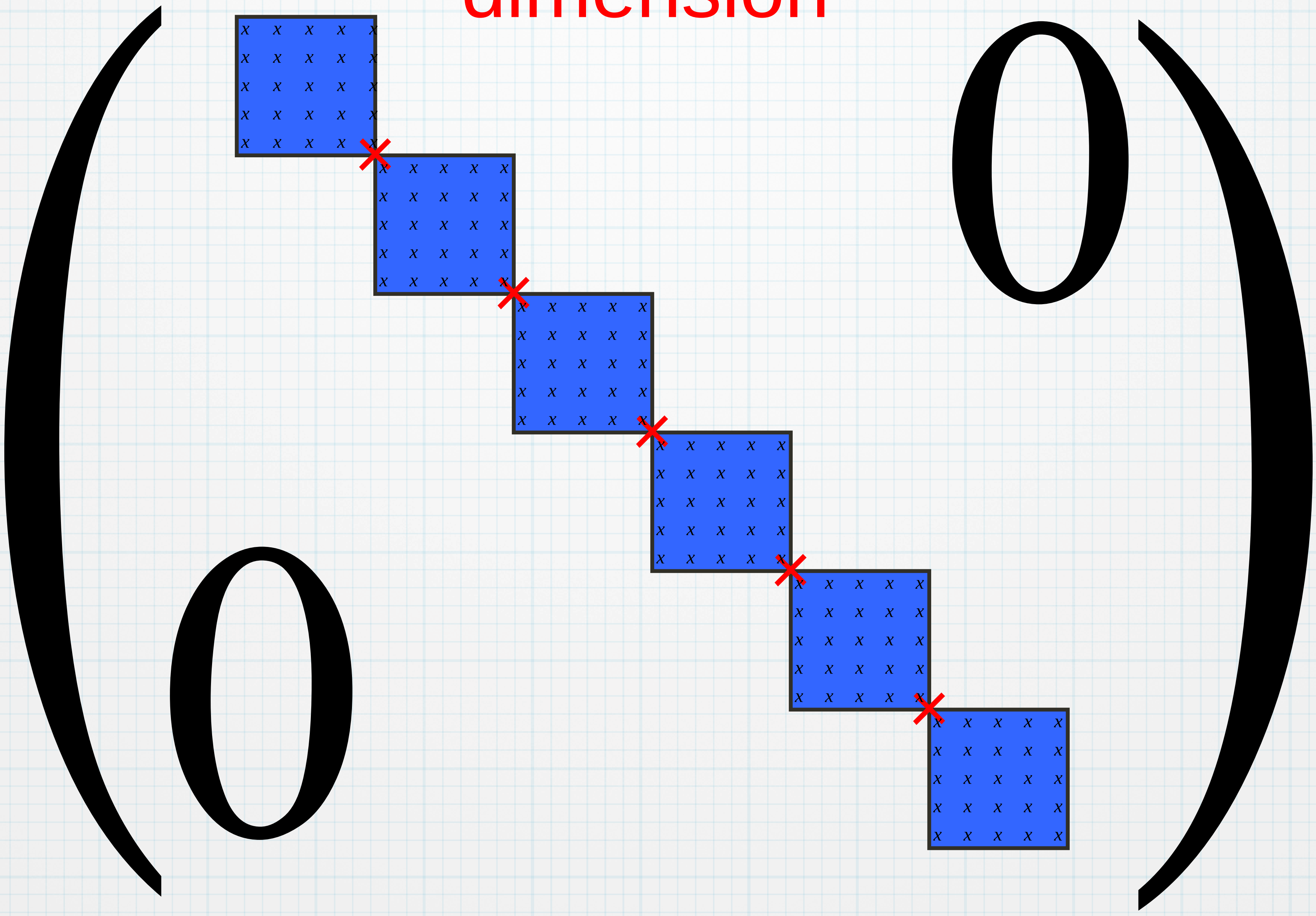
* Only function continuity enforced at the element boundaries **– Is that legal** ?

Gauss-Lobatto quadrature rule - Common end points

$$F_n^i(x) = \frac{(f_n^i(x) + f_1^{i+1}(x))}{(\sqrt{w_n^i} + \sqrt{w_1^{i+1}})}$$

1 Sparse representation
2. Spectral Accuracy
3. Matrix elements easily constructed from subelements

FEDVR Matrix Structure in one dimension



One Effective Approach to Time Propagation Methods

* Short Iterative Lanczos

$$U(t_0+\Delta t, t_0) \approx \exp[-i\frac{\mathbf{H}(t_0)\Delta t}{\hbar}]$$

Diagonalize Hamiltonian in Krylov basis

$$\beta_{n+1}|n+1 >= [\mathbf{H}(t_0) - \alpha_n]|n > -\beta_n|n-1 >$$

$$|q_n > \quad = \quad [\mathbf{H}(t_0) - \alpha_n]|n > -\beta_n|n-1 >$$

$$\beta_{n+1} \quad = \quad \sqrt{< q_n|q_n >}$$

- Few recursions needed for short time- Typically 10 to 20 via adaptive time stepping

$$< \psi_q|\exp[-i\frac{\mathbf{H}(t_0)\Delta t}{\hbar}]|\psi_{q'} >= \sum_n < \psi_q|n > \exp[-i\frac{E_n(t_0)\Delta t}{\hbar}] < n|\psi_{q'} >$$

- Unconditionally stable
- Major step - matrix vector multiply, a few scalar products and diagonalization of tri-diagonal matrix

The Basic Equations for He

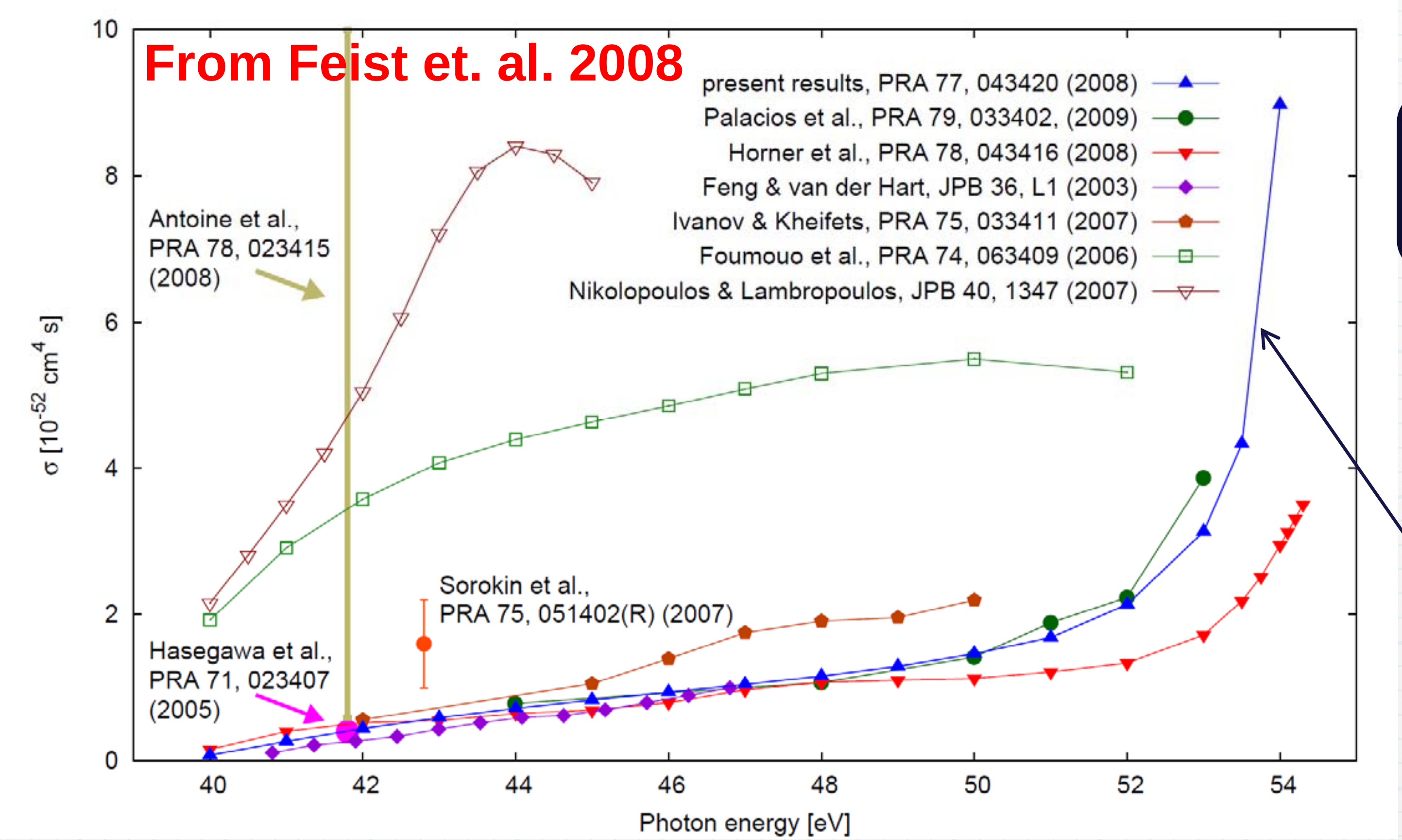
$$\Psi(\mathbf{r_1},\mathbf{r_2},t)=\sum_{L,M}^{\infty}\sum_{l_1,l_2}^{\infty}\frac{R^{LM}_{l_1.l_2}(r_1,r_2,t)}{r_1r_2}\mathcal{Y}^{LM}_{l_1,l_2}(\Omega_1,\Omega_2)$$

$$\mathcal{Y}^{LM}_{l_1l_2}(\Omega_1,\Omega_2)=\sum_{m_1,m_2}<l_1m_1l_2m_2|LM>Y_{l_1m_1}(\Omega_1)Y_{l_2m_2}(\Omega_2)$$

$$i\frac{\partial}{\partial t}R^{LM}_{l'_1,l'_2}(r_1,r_2,t)=\sum_{L,M}^{\infty}\sum_{l_1,l_2}^{\infty}<l'_1l'_2L'M'|\mathbf{H}|l_1l_2LM>R^{LM}_{l_1,l_2}(r_1,r_2,t)$$

M
conserved
for linearly
polarized
light

Comparison of Theoretical and Available Experimental Results -Total X-Sect



From Feist et. al. 2008

Considerable discrepancies!

Rise at sequential threshold

Extensive convergence tests:

angular momenta, radial grid, pulse duration (up to 20 fs),

time after pulse (propagate electrons to asymptotic region)

→ error below 1%

$$T_{eff,N} = \int_{-\infty}^{\infty} dt \left(\frac{I(t)}{I_0}\right)^N$$

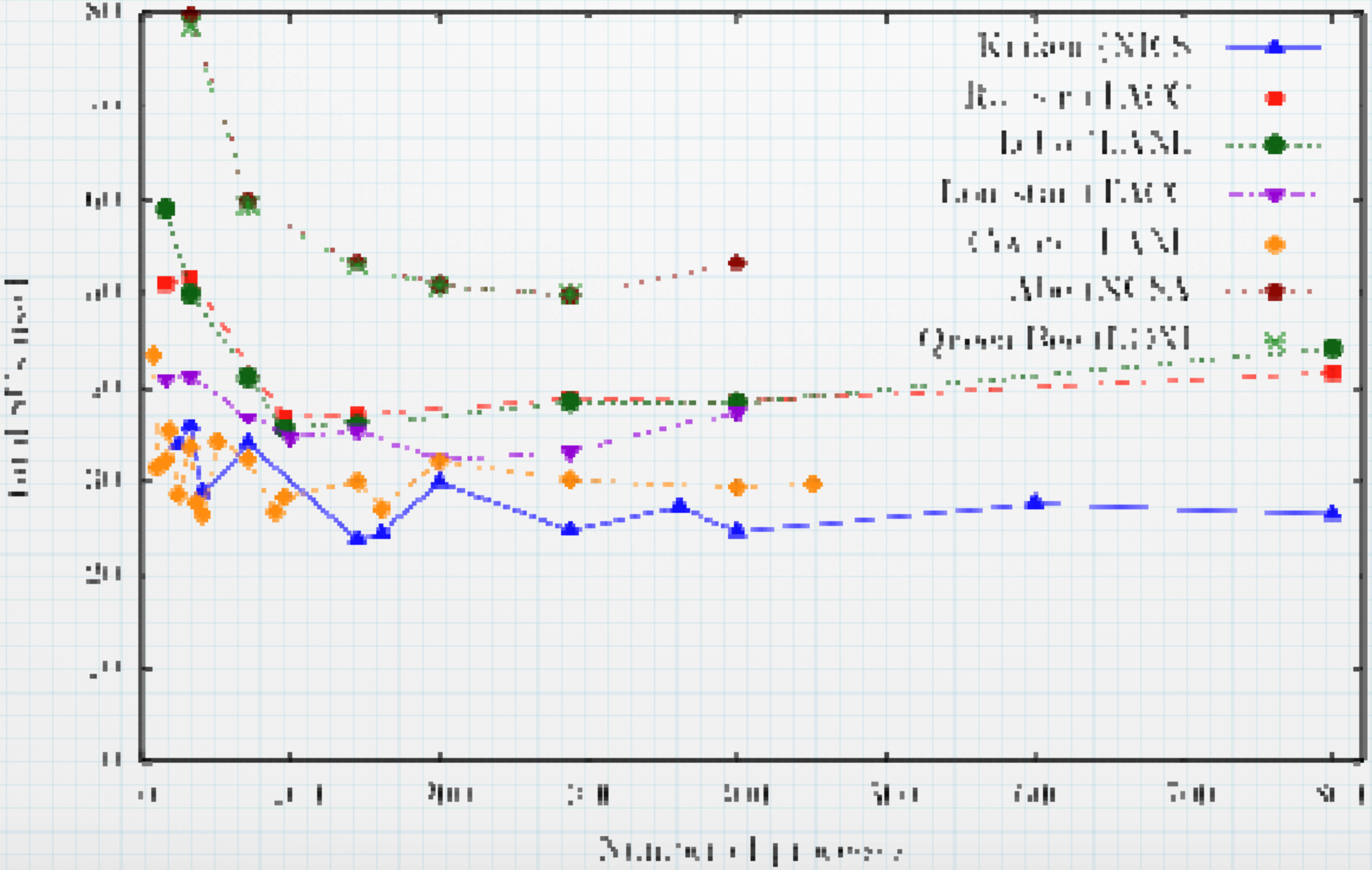
$$\sigma_N \approx \left(\frac{\omega}{I_0}\right)^N \frac{1}{T_{eff,N}} \int\int\int\int dE_1 dE_2 d\Omega_1 d\Omega_2 P^{DI}(E_1, E_2, \Omega_1, \Omega_2)$$

Performance on Various Mutiprocessors

Table 1: Performance of the He FEDVR code on various platforms.

Name	CPU's	GHz	cores/CPU	CPU's/cores per node
Coyote	Opteron	2.60	1	2/2
Lobo	Opteron	2.20	4	4/16
Ranger	Opteron	2.30	4	4/16
Lonestar	Xeon	2.66	2	2/4
Abe	Xeon	2.33	4	2/8
Queen Bee	Xeon	2.33	4	2/8
Kraken	Opteron	2.33	4	2/8

Bartschat et. al.
XSEDE Proposal

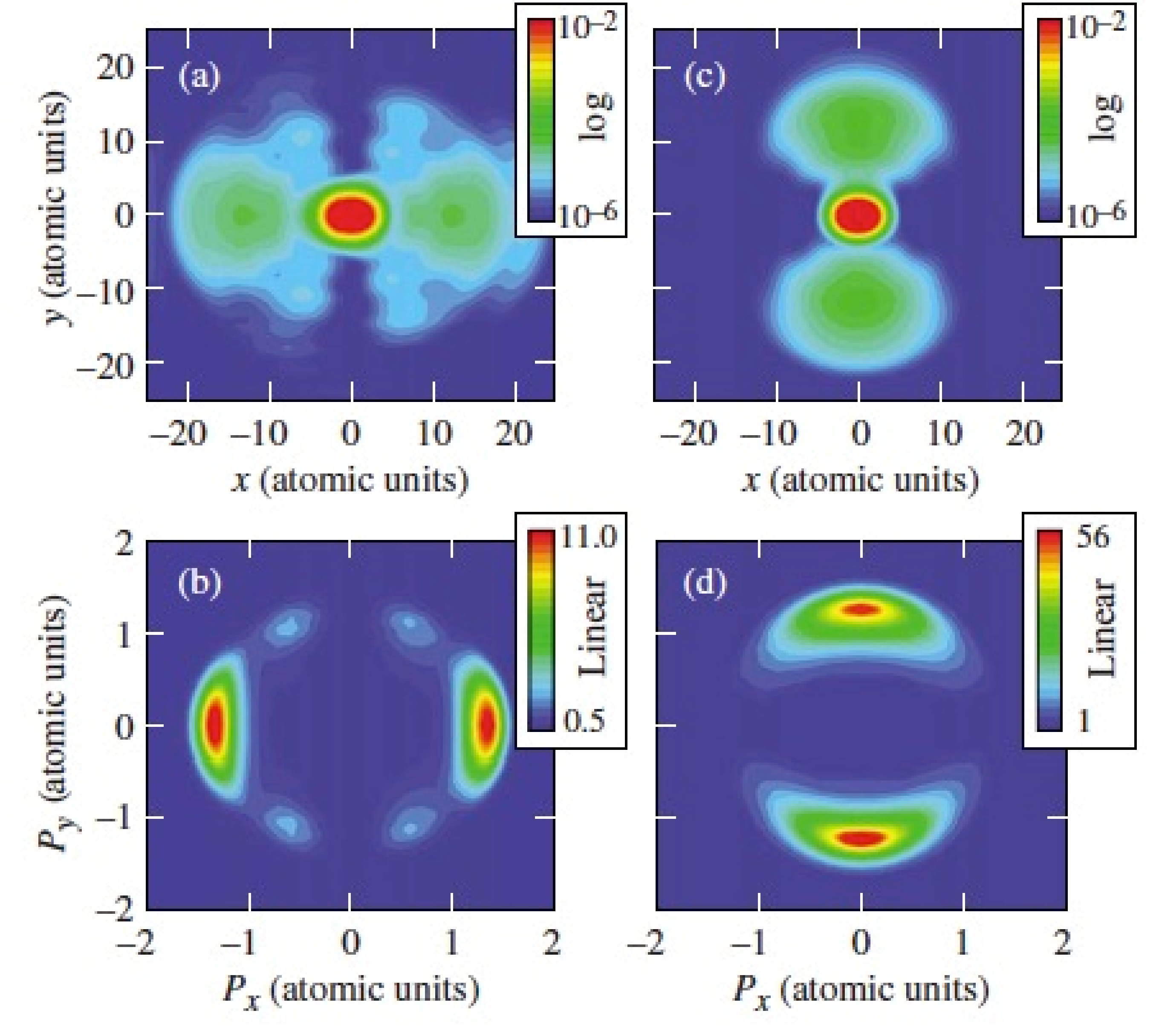


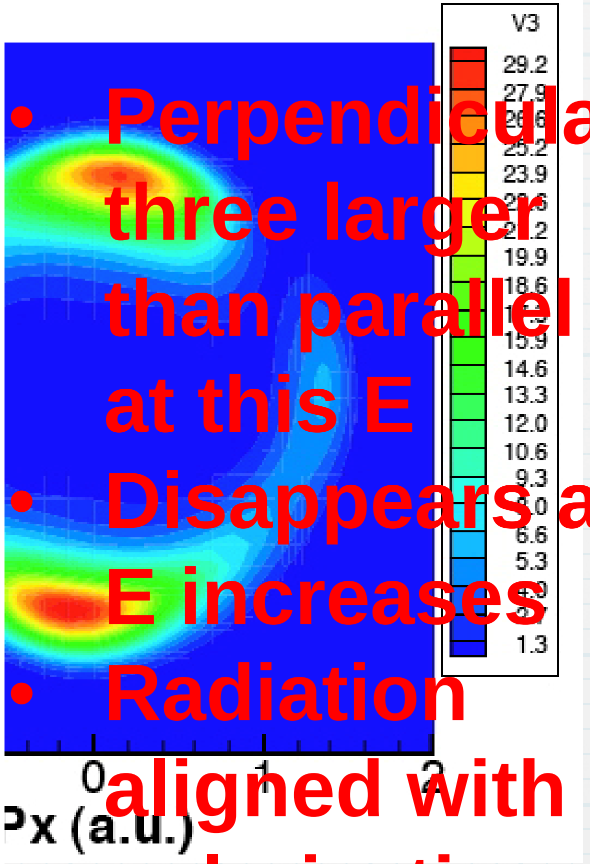
Conclusion

- Definition of T_eff is correct for Non-Sequential DI process
- Total X-sections can be extracted properly using Coulomb projection - At long times and large distances the wavepacket consists of a superposition of stationary states with the electrons WELL SEPARATED
- Pulse shape affects resolution
- Total X-section not very sensitive to angular momentum included

Quantum Interference Effects in H_2^+

50ev
500as





- **Perpendicular three larger than parallel at this E**
- **Disappears as E increases**
- **Radiation aligned with polarization**

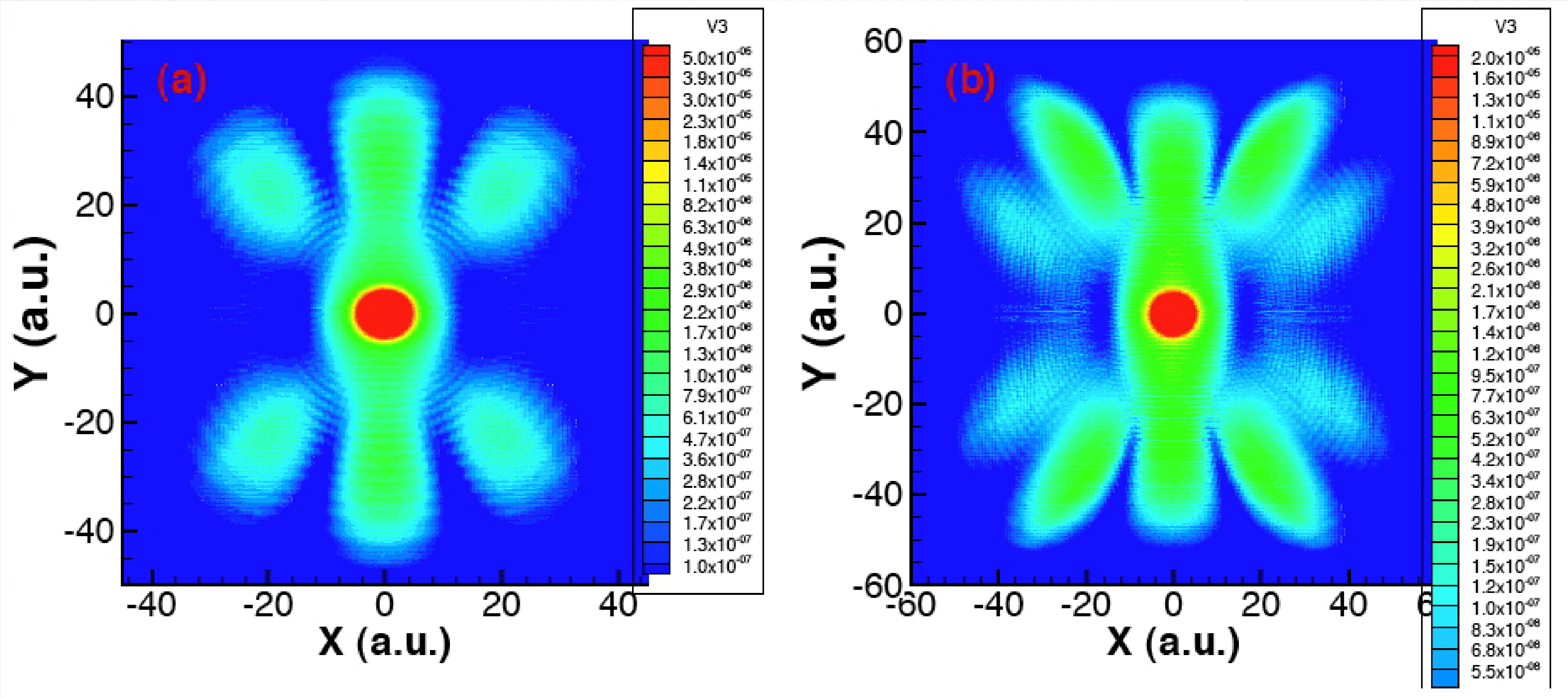
Momentum Distribution

arization – result of
l polarizations having
differing probabilities

Quantum Interference Effects in $\mathbf{H_2^+}$

Photon energy =350eV

Photon energy =630eV



Classical double slit distribution

Non classical distribution

- Final Probability density for perpendicular polarization
- Note second order effects at higher E but not “classical”

Interference path vs R Critical Factor

Final Remarks

- Computation in AMO physics play a critical role in understanding many complex process that result from the interplay of "simple" interactions
- The development of efficient and often novel algorithms are required to make progress.

Thanks to Los Alamos National Laboratory, The US National Science Foundation and the National Institute of Standards and Technology for supporting me to do what I enjoy for 45 years

- Access to high performance computing facilities enables us to push our methods to the limits and produce results in many cases that are more accurate than experiment

Personally, I have found doing this kind of science challenging and extremely rewarding – I have met and worked with some wonderful and pretty smart folks. - I hope you come away with a similar feeling AND I hope can continue doing what I enjoy a while longer