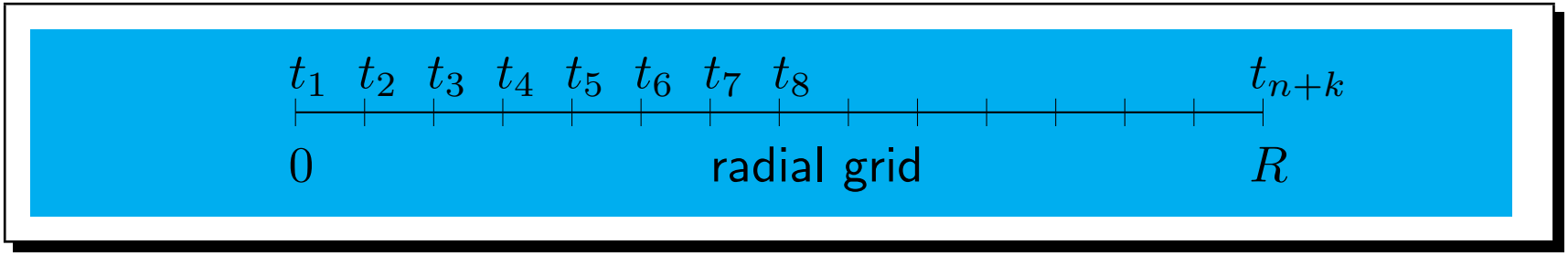
B-Spline Basis Sets in Relativistic Many-Body Calculations

W.R. Johnson
Department of Physics, 225 Nieuwland Science Hall
University of Notre Dame, Notre Dame, IN 46556

The use of linear combinations of B-splines to obtain finite basis sets for the Dirac equation is reviewed and applications of B-spline basis sets to many-body perturbation theory, the Dyson equation for negative ions, configuration interaction calculations and electron scattering are described.

UNIVERSITY OF NOTRE DAME

What are B-Splines?



Divide the radial axis $0 \leq r \leq R$ into intervals defined by the knot sequence $0 = t_1 \leq t_2 \leq t_3 \leq \cdots \leq t_{n+k} = R$. The B-splines of order k on this knot sequence are defined by the recursion relations:

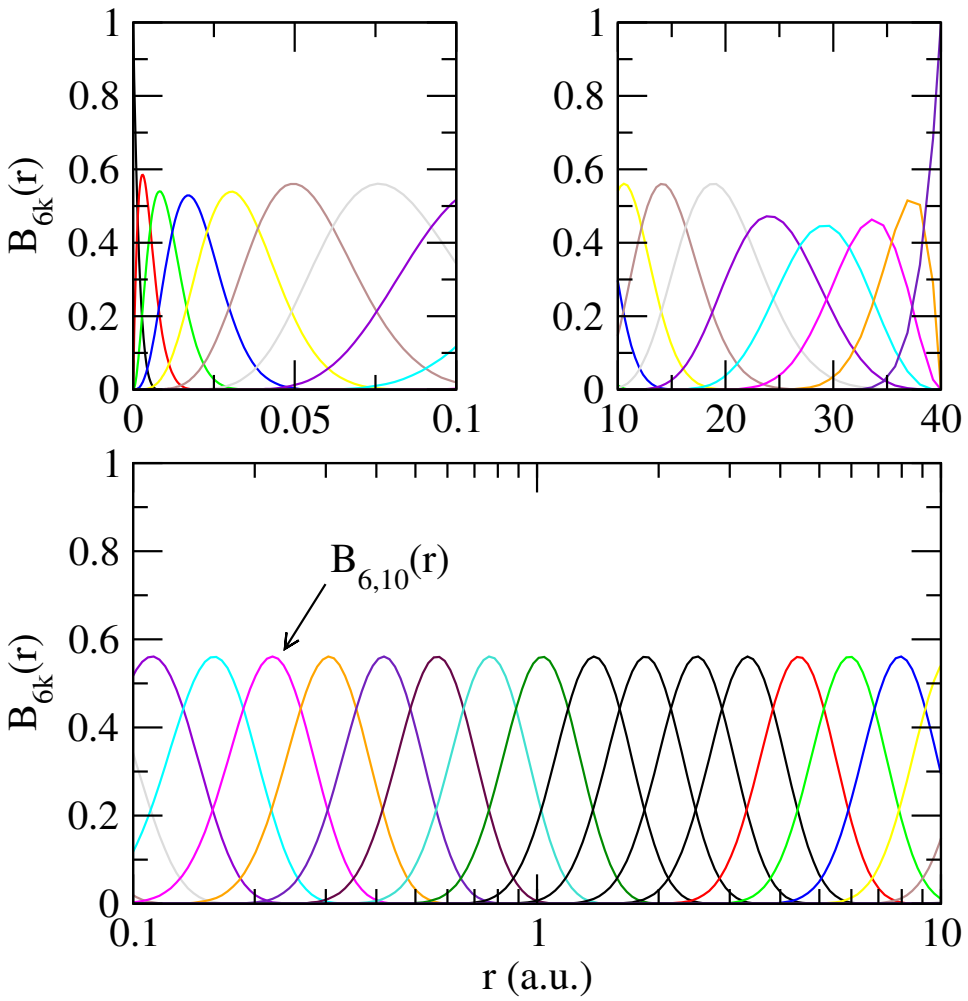
$$B_{i,1}(r) = \begin{cases} 1, & t_i \leq r < t_{i+1}, \\ 0, & \text{otherwise}, \end{cases}$$

and

$$B_{i,k}(r) = \frac{r - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(r) + \frac{t_{i+k} - r}{t_{i+k} - t_{i+1}} B_{i+1,k-1}(r) \ .$$

The function $B_{i,k}(r)$ is a piecewise polynomial of degree $k - 1$ inside the interval $t_i \leq r < t_{i+k}$ and $B_{i,k}(r)$ vanishes outside this interval.

Example: B-Splines on an "Atomic" Grid



How are Basis Functions Obtained?

1) Confine atom to large cavity: discrete+continuous $\longrightarrow$ discrete.

2) Expand orbitals in a finite basis set: infinite spectrum $\longrightarrow$ finite.

3) Use B-splines to form the finite basis.

Start from the action functional for the Dirac equation:

$$S = \int_0^R dr \left\{ c \left[P\frac{dQ}{dr} - Q\frac{dP}{dr} + \left(\frac{2\kappa}{r}\right) PQ \right] + \left(P^2 + Q^2\right) V(r) - c^2 Q^2 \right\}$$

$\delta(S - \lambda N) = 0 \Rightarrow$ radial Dirac equation. Expand the radial Dirac orbitals in B-splines.

$$P(r) = \sum_{i=1}^{n} p_i B_{ik}(r) \qquad Q(r) = \sum_{i=1}^{n} q_i B_{ik}(r)$$

then $S - \lambda N$ becomes a quadratic form in p_i, q_i and variational condition leads to a generalized eigenvalue equation for the vector $v = (p_1, p_2, \cdots, q_1, q_2, \cdots)$.

Generalized Eigenvalue Equation for Basis Orbitals

$$Av = \lambda Bv$$

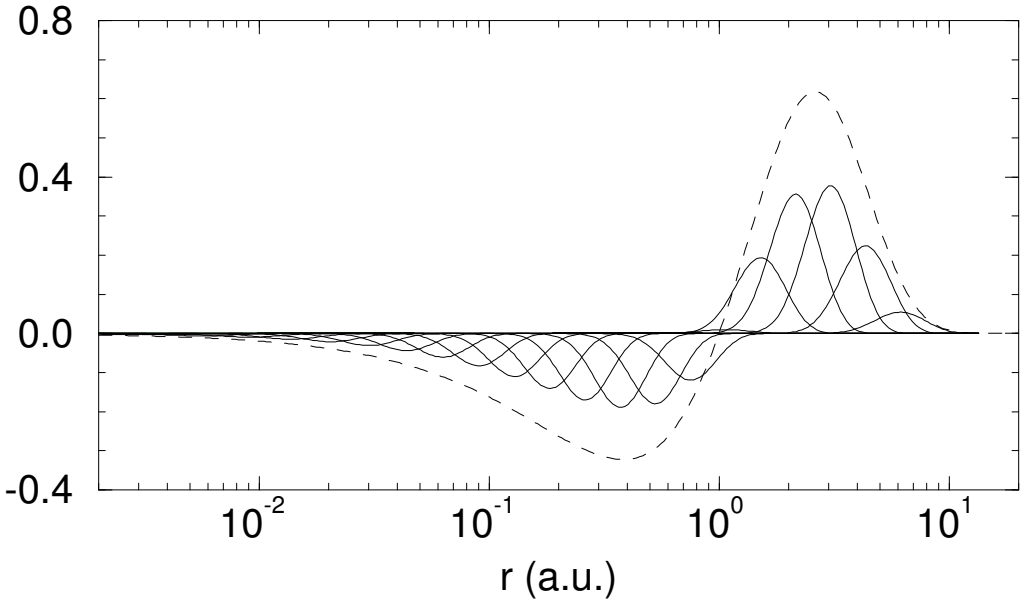
where A and B are symmetric, *diagonally dominant*, $2n \times 2n$ matrices. We obtain n positive solutions for energies $> -2mc^2$ (bound-state and electron scattering states) and n solutions for energy $< -2mc^2$ (positron states).

- The reconstructed orbitals are precisely orthogonal.
- The spectrum splits precisely: $1/2$ electron states – $1/2$ positron states.
- Energies of low-lying states agree with "free-space" energies.
- Energy-weighted sum rules (e.g. TRK rule) satisfied precisely.

Example: B-spline energies for Cs [n=50,k=9,R=50]

n	DHF	B-spline	DHF	B-spline	DHF	B-spline
	$s_{1/2}$		$p_{1/2}$		$p_{3/2}$	
1	-1330.118917	-1330.118530				
2	-212.564461	-212.564413	-199.429431	-199.429429	-186.436550	-186.436550
3	-45.969741	-45.969731	-40.448293	-40.448293	-37.894301	-37.894301
4	-9.512822	-9.512820	-7.446284	-7.446284	-6.921001	-6.921001
5	-1.489806	-1.489806	-0.907898	-0.907898	-0.840340	-0.840340
6	-0.127368	-0.127368	-0.085616	-0.085616	-0.083785	-0.083785
7	-0.055187	-0.055187	-0.042021	-0.042021	-0.041368	-0.041367
	$d_{3/2}$		$d_{5/2}$		$f_{5/2}$	
3	-28.309496	-28.309496	-27.775153	-27.775153		
4	-3.485618	-3.485619	-3.396901	-3.396901	-0.031274	-0.031269
5	-0.064420	-0.064420	-0.064530	-0.064530	-0.020019	-0.019325
6	-0.036087	-0.036085	-0.036090	-0.036088	-0.013903	-0.007673
7	-0.022622	-0.022123	-0.022613	-0.022111		
	$f_{7/2}$		$g_{7/2}$		$g_{9/2}$	
4	-0.031273	-0.031270				
5	-0.020020	-0.019326	-0.020000	-0.019776	-0.020000	-0.019776
6	-0.013903	-0.007675	-0.013889	-0.010634	-0.013889	-0.010634

Sample B-spline Basis Orbital



$P_{2s}(r)$ basis function in a Coulomb potential with Z =2.

Example: TDHF (RPA) for Closed-Shell Atoms

Apply a frequency-dependent perturbation to the atom $V^+e^{-i\omega t} + V^-e^{i\omega t}$

$$\phi_a e^{-i\epsilon a t} \rightarrow \phi_a e^{-i\epsilon a t} + \phi_a^+ e^{-i(\epsilon a+\omega)t} + \phi_a^- e^{-i(\epsilon a-\omega)t}$$

$$(h_{\mathsf{HF}} - \epsilon_a - \omega)\phi_a^+ + \Delta V_{\mathsf{HF}}^+ \phi_a = -V^+\phi_a$$

$$(h_{\mathsf{HF}} - \epsilon_a + \omega)\phi_a^- + \Delta V_{\mathsf{HF}}^- \phi_a = -V^-\phi_a$$

The homogeneous equations $\left[V^\pm = 0\right]$ lead to an eigenvalue system for ω. The solutions are the (dipole, quadrupole, etc.) excitation frequencies and the associated excited states of the atom. Expand the functions $\phi_a^\pm$ for the dipole case in a basis set and solve. (e.g. Expand the nonrelativistic $1s, 2s, 3s, 2p, 3p$ orbitals for Argon using 40 splines. The number of expansion coefficients required is 3×38+2×40+2×37=268. We expect to find 268 frequencies and 268 sets $\phi_a^\pm$.) One can use the resulting frequencies and perturbed orbitals to check sum rules (TRK) and calculate properties (α, R^2, C_6) of the closed-shell atom.

2nd- and 3rd-order MBPT

No-Virtual Pair Approximation[1]

$$H = \sum_i \epsilon_i a_i^\dagger a_i + \frac{1}{2}\sum_{ijkl} v_{ijkl} a_i^\dagger a_j^\dagger a_l a_k - \sum_{ij} U_{ij} a_i^\dagger a_j,$$

where indices (i, j, k, l) run over electron states only.

$$E^{(2)} = -\frac{1}{2}\sum_{mnab} \frac{\tilde{v}_{abmn} v_{mnab}}{\epsilon_m + \epsilon_n - \epsilon_a - \epsilon_b}$$

$$E^{(3)} = \sum_{abcmnr} \frac{\tilde{v}_{acnr}\tilde{v}_{nmba}\tilde{v}_{rbmc}}{(\epsilon_{nm} - \epsilon_{ab})(\epsilon_{rn} - \epsilon_{ac})} + \text{two more terms}$$

[1] Brown & Ravenhall, Proc. Roy. Soc. A **208**, 552 (1951).

MBPT for Li-like U (eV)

Term	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$
$E^{(0+1)}$	-32917.9662	-32631.2771	-28403.1054
$E^{(2)}$	-0.2915	-0.8342	-0.3339
$E^{(3)}$	-0.0009	-0.0022	-0.0013
Breit	34.6596	71.2971	18.4470
RM + MP	0.0759	-0.0411	-0.0289
Total	-32883.5232	-32561.1400	-28384.9646
Transition Energy		$2s_{1/2} - 2p_{1/2}$	$2s_{1/2} - 2p_{3/2}$
MBPT		322.38	4498.56
Expt.[a]		280.59(10)	4459.37(21)
Expt. - MBPT		-41.79(10)	-39.19(21)
Lamb Shift Calc.[b]		-41.77	-39.13(5)

(a) Schweppe et al. PRL **66**, 1434 (1991); Beiersdorfer et al. PRL **71**, 3939 (1993).
(b) S. A. Blundell, PRA **47**, 1790 (1993); Yerokhin et al. PRA **60**, 3522 (1999).

Transition Matrix Elements

Consider a monovalent atom: The line strength for a transition $v \rightarrow w$ is $S = |Z_{wv}|^2$ where, in lowest order, $Z_{wv} = \langle w \| z \| v \rangle$. In higher order

$$Z_{wv} \rightarrow Z_{wv}^{(1)} + Z_{wv}^{(2)} + Z_{wv}^{(3)}$$

$$Z_{wv}^{(2)} = \sum_{ma} \frac{Z_{am}^{(1)} \tilde{v}_{wmva}}{\epsilon_a - \epsilon_m - \omega} + \sum_{ma} \frac{\tilde{v}_{wavm} Z_{ma}^{(1)}}{\epsilon_a - \epsilon_m + \omega}$$

$$Z_{wv}^{(3)} = 16 \text{ RPA} + 8 \text{ Brueckner} + 36 \text{ St Rad} + 4 \text{ norm}$$

Replace $Z^{(1)}$ by Z^{RPA} and one can prove gauge independence (L=V) through 3rd-order. (I. Savukov)

Negative Ions

Example: closed-shell atom + one electron. Problem: no lowest-order bound state. Perturbation theory doesn't work!

Solution: Start from the Dyson equation

$$(H + V_{\text{HF}} - E)\,\Psi(\boldsymbol{r}) = -\int \Sigma(\boldsymbol{r}, \boldsymbol{r}')\Psi(\boldsymbol{r}')d^3r'.$$

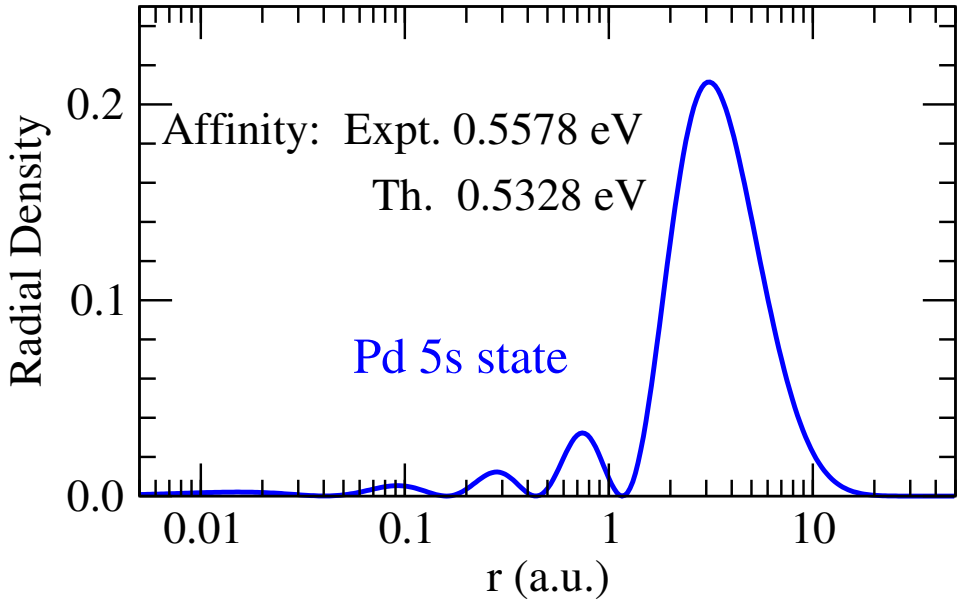
Σ is the "self-energy" or "polarization" operator: $\langle v|\Sigma|v\rangle = E - E^{(0)}$. Expand Ψ in a B-spline basis $[\Psi = \sum_i c_i\psi_i]$ and Dyson equation becomes

$$E\,c_i = \sum_j \Big[(\Sigma)_{ij} + \epsilon_i\delta_{ij}\Big]\,c_j.$$

Eigenvalues of Dyson equation give exact energies of the negative ion!

Negative Pd ($1s^2 \cdots 4d^{10}$) Ion with $\Sigma \rightarrow \Sigma^{(2)}$

i	c_i	i	c_i	i	c_i	i	c_i
1	0.0000	6	0.5570	11	-0.1634	16	-0.0097
2	0.0000	7	0.4620	12	-0.1325	17	-0.0020
3	-0.0003	8	0.3442	13	-0.0312	18	0.0002
4	-0.0032	9	-0.2543	14	-0.0741	19	-0.0000
5	0.4588	10	-0.1757	15	-0.0314	20	-0.0000



Relativistic CI Calculations

Example: He-like ions

$$\Phi_{ab}^{JM} = \eta_{ab} \sum_{m_a m_b} \langle j_a m_a, j_b m_b | JM \rangle a_a^\dagger a_b^\dagger |0\rangle$$

$$\Psi^{JM} = \sum_{ab} C_{ab} \Phi_{ab}^{JM}$$

Variational Principle $\Rightarrow EC_{ab} = \sum_{cd} \langle ab|H|cd\rangle C_{cd}$

Example $^3P_0$ states.

a	b	$n_a \times n_b$	Size
$n_a s_{1/2}$	$n_b p_{1/2}$	40×40	1600
$n_a p_{3/2}$	$n_b d_{3/2}$	40×40	3200
$n_a d_{5/2}$	$n_b f_{5/2}$	40×40	4800
$n_a f_{7/2}$	$n_b g_{7/2}$	40×40	6400
$\vdots$		$\vdots$	$\vdots$

Sample CI results

- **spline basis:** We need all eigenvectors and eigenvalues of $(2l_{\max}+1)\times 80\times 80$ symmetric matrices. We use the routine DSTGV from the LAPACK library for this step.
- **2-particle matrix:** (a) Set up H-matrix. (b) Use Davidson's Method[2] to obtain the first few eigenvectors.

$2\,^3\mathrm{P}_0 - 2\,^3\mathrm{S}_1$ Energy Interval (cm^{-1})

Z	CI + QED	Expt.	Z	CI + QED	Expt.
5	35393.61(3)	35393.627(13)	12	95847.7	95850.6(7.3)
6	43898.7	43899(1)	14	113809	113815(4)
7	52420.4	52420.0(1.1)	16	132219	132218(4)
8	60978.7	60978.4(0.5)	18	151156	151204(9)
9	69590.8	69590.9(3.4)	26	233471	232558(550)
10	78263.4	78263.2(2.5)	36	356828	357400(260)

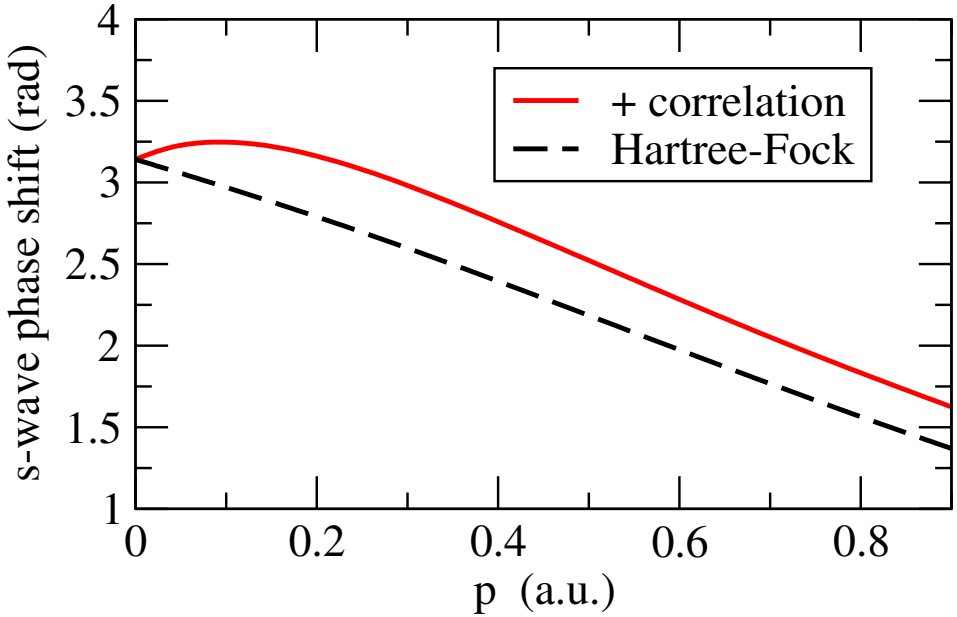
[2] A. Stathopoulos & CF Fischer, Comp. Phys. Comm. **79** 268 (1994).

Electron-Xe (or He, Ne, Kr, $\cdots$) Scattering

Including correlation, $\delta_\kappa^{(\mathrm{HF})}(p) \rightarrow \delta_\kappa^{(\mathrm{HF})}(p) + \Delta\delta_\kappa(p)$, where

$$\sin\left[\Delta\delta_\kappa(p)\right] = -\pi\langle\phi_\kappa^{(\mathrm{HF})}|\Sigma|\phi_\kappa^{(\mathrm{HF})}\rangle.$$

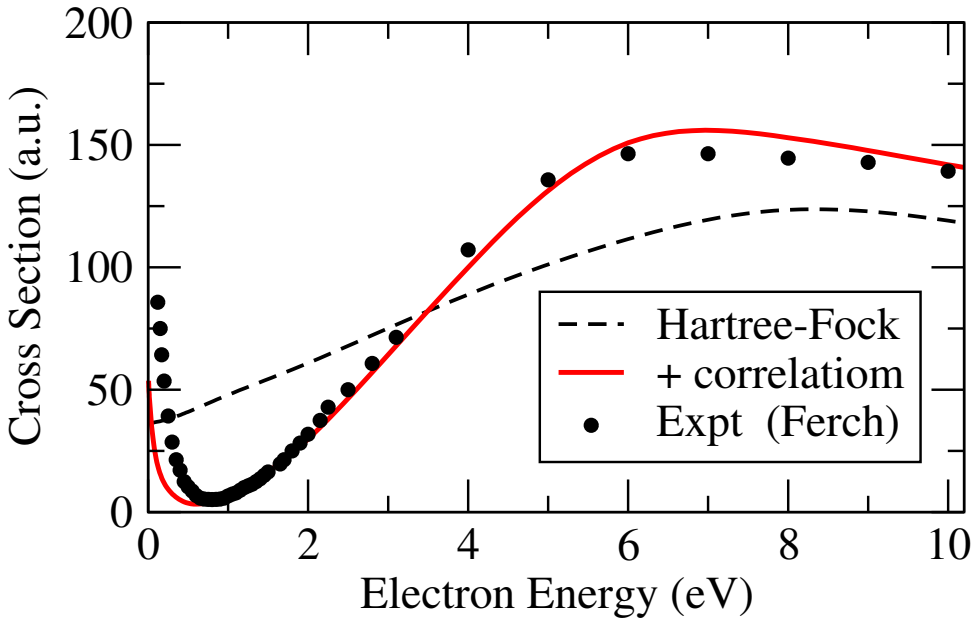
Evaluate matrix elements with $\Sigma = \Sigma^{(2)}$ using a B-spline basis.



Ramsauer Effect in e-Xe Scattering

Cross section:

$$\sigma(p) = \frac{\pi}{p^2} \sum_{\kappa} |\kappa| \sin^2 \delta_\kappa$$



Other Applications of B-Splines

- Photoionization of Alkali-Metals: Derevianko, Savukov, Johnson
- Large-Scale CI: Cheng, Chen, Johnson
- Mixed CI+MBPT: Koslov, Dzuba, Safronova, Savukov, Johnson
- Gauge-Independent MBPT Transition Amplitudes: Savukov, Johnson
- SD(T) Coupled Cluster: Pal, Safronova, Derevianko, Porsev, Johnson
- PNC in Cesium and Thallium: Sapirstein, Blundell, Safronova, Derevianko, Johnson
- 4th-order MBPT: Deverianko, Porsev
- PNC in Francium & Anapole Moments: Safronova, Johnson
- Lamb Shift: Blundell, Snyderman
- Breit Corrections to PNC: Derevianko, Dzuba, Johnson
- Radiative Corrections to PNC: Soff, Dzuba, Flambaum, Johnson
- Isotope Shifts: Safronova, Dzuba, Johnson
- Polarizabilities and C_6 Coefficients: Safronova, Derevianko, Babb, Johnson
- Black-Body Correction to Cs Clock: Derevianko, Safronova, Dzuba, Flambaum

Excellent Review: H. Bachau et al., Rep. Prog. Phys. **64**, 1815 (2001).