B-Spline Basis Sets in Relativistic Many-Body Calculations

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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.
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

![Graphs showing B-Splines on an "Atomic" Grid](image-url)
How are Basis Functions Obtained?

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

2) Introduce finite basis: infinite spectrum $\to$ 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.

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

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, \textit{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 precisely with “free-space” energies.
- Energy-weighted sum rules (e.g. TRK rule) satisfied precisely.
$P_{2s}(r)$ basis function in a Coulomb potential with $Z = 2$. 
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.

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

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

**MBPT for Li-like U (eV)**

<table>
<thead>
<tr>
<th>Term</th>
<th>$2s_{1/2}$</th>
<th>$2p_{1/2}$</th>
<th>$2p_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^{(0+1)}$</td>
<td>-32917.9662</td>
<td>-32631.2771</td>
<td>-28403.1054</td>
</tr>
<tr>
<td>$E^{(2)}$</td>
<td>-0.2915</td>
<td>-0.8342</td>
<td>-0.3339</td>
</tr>
<tr>
<td>$E^{(3)}$</td>
<td>-0.0009</td>
<td>-0.0022</td>
<td>-0.0013</td>
</tr>
<tr>
<td>Breit</td>
<td>34.6596</td>
<td>71.2971</td>
<td>18.4470</td>
</tr>
<tr>
<td>RM + MP</td>
<td>0.0759</td>
<td>-0.0411</td>
<td>-0.0289</td>
</tr>
<tr>
<td>Total</td>
<td>-32883.5232</td>
<td>-32561.1400</td>
<td>-28384.9646</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Transition Energy</th>
<th>$2s_{1/2} - 2p_{1/2}$</th>
<th>$2s_{1/2} - 2p_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBPT</td>
<td>322.38</td>
<td>4498.56</td>
</tr>
<tr>
<td>Expt.$^a$</td>
<td>280.59(10)</td>
<td>4459.37(21)</td>
</tr>
<tr>
<td>Expt. - MBPT</td>
<td>-41.79(10)</td>
<td>-39.19(21)</td>
</tr>
<tr>
<td>Lamb Shift Calc.$^b$</td>
<td>-41.77</td>
<td>-39.13(5)</td>
</tr>
</tbody>
</table>

b) S. A. Blundell, PRA 47, 1790 (1993); Yerokhin et al. PRA 60, 3522 (1999).
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

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

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

\[
Ec_i = \sum_j \left[ (\Sigma)_{ij} + \epsilon_i \delta_{ij} \right] c_j.
\]

Eigenvalues of Dyson equation give exact energies of the negative ion!
Palladium Ion with $\Sigma \rightarrow \Sigma^{(2)}$

<table>
<thead>
<tr>
<th>$i$</th>
<th>$c_i$</th>
<th>$i$</th>
<th>$c_i$</th>
<th>$i$</th>
<th>$c_i$</th>
<th>$i$</th>
<th>$c_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0000</td>
<td>6</td>
<td>0.5570</td>
<td>11</td>
<td>-0.1634</td>
<td>16</td>
<td>-0.0097</td>
</tr>
<tr>
<td>2</td>
<td>0.0000</td>
<td>7</td>
<td>0.4620</td>
<td>12</td>
<td>-0.1325</td>
<td>17</td>
<td>-0.0020</td>
</tr>
<tr>
<td>3</td>
<td>-0.0032</td>
<td>8</td>
<td>0.3442</td>
<td>13</td>
<td>-0.0312</td>
<td>18</td>
<td>0.0002</td>
</tr>
<tr>
<td>4</td>
<td>-0.0032</td>
<td>9</td>
<td>-0.2543</td>
<td>14</td>
<td>-0.0741</td>
<td>19</td>
<td>-0.0000</td>
</tr>
<tr>
<td>5</td>
<td>0.4588</td>
<td>10</td>
<td>-0.1757</td>
<td>15</td>
<td>-0.0314</td>
<td>20</td>
<td>-0.0000</td>
</tr>
</tbody>
</table>

Affinity: Expt. 0.5578 eV
Th. 0.5328 eV

Radial Density

Pd 5s state
Relativistic CI Calculations

Example: He-like ions

\[ \Phi_{ab}^{JM} = \eta_{ab} \sum_{m_a m_b} \langle j_a m_a, j_b m_b \mid J M \rangle a_a^\dagger a_b^\dagger \mid 0 \rangle \]

\[ \Psi^{JM} = \sum_{ab} C_{ab} \Phi_{ab}^{JM} \]

Variational Principle \( \Rightarrow \) \( EC_{ab} = \sum_{cd} \langle ab \mid H \mid cd \rangle C_{cd} \)

Example \( ^3P_0 \) states.

<table>
<thead>
<tr>
<th>( i )</th>
<th>( j )</th>
<th>( n_i \times n_j )</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_i s_{1/2} )</td>
<td>( n_j p_{1/2} )</td>
<td>( 40 \times 40 )</td>
<td>1600</td>
</tr>
<tr>
<td>( n_i p_{3/2} )</td>
<td>( n_j d_{3/2} )</td>
<td>( 40 \times 40 )</td>
<td>3200</td>
</tr>
<tr>
<td>( n_i d_{5/2} )</td>
<td>( n_j f_{5/2} )</td>
<td>( 40 \times 40 )</td>
<td>4800</td>
</tr>
<tr>
<td>( n_i f_{7/2} )</td>
<td>( n_j g_{7/2} )</td>
<td>( 40 \times 40 )</td>
<td>6400</td>
</tr>
<tr>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
</tr>
</tbody>
</table>
Sample CI results

- **spline basis:** We need all eigenvectors and eigenvalues of \((2l_{\text{max}} + 1) \times 80 \times 80\) 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.

\[
2^3P_0 - 2^3S_1 \text{ Energy Interval (cm}^{-1}\text{)}
\]

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

Electron Scattering

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

\[
\sin [\Delta \delta_\kappa(p)] = -\pi \langle \phi^{(HF)}_\kappa \rvert \Sigma \lvert \phi^{(HF)}_\kappa \rangle.
\]

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