The Herman-Skillman method

The radial Hartree-Fock equations are:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Where the *Pi*(*r*) are the *r*-multiplied radial wave functions

|  |  |  |
| --- | --- | --- |
|  |  |  |

Which are normalized such that

|  |  |  |
| --- | --- | --- |
|  |  |  |

The volume integral of the *Rn,l*(*r*) wave functions is the total charge:

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

Define the exchange potential *Vex*(*r*) as:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Define the full potential *V*(*r*):

|  |  |  |
| --- | --- | --- |
|  |  |  |

Substituting into (1) gives:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Multiply through by -2*m*/ *ħ*2:

|  |  |  |
| --- | --- | --- |
|  |  |  |

In Rydberg units (*ħ* = 2*m*e = *e*2/2 = 1), the radial equation is:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Where

|  |  |  |
| --- | --- | --- |
|  |  |  |

In the central field approximation (following Herman and Skillman),

|  |  |  |
| --- | --- | --- |
|  |  |  |

Where the radial charge density is

|  |  |  |
| --- | --- | --- |
|  |  |  |

And the spherically averaged radial charge density is

|  |  |  |
| --- | --- | --- |
|  |  |  |

Note the form of the exchange potential *Vex*(*r*)

|  |  |  |
| --- | --- | --- |
|  |  |  |

The r-multiplied radial potential *U*(*r*) is

|  |  |  |
| --- | --- | --- |
|  |  |  |

The r-multiplied exchange potential is:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Substituting sigma for rho:

|  |  |  |
| --- | --- | --- |
|  |  |  |

# Solving for *Pnl*(*r*) with Numerov’s algorithm

Numerov’s method is useful for solving DEs of the form:

|  |  |  |
| --- | --- | --- |
|  |  |  |

In our case,

With the additional boundary conditions that

{need another boundary condition here to ensure unique solution to within a constant}

Which can be numerically solved using Numerov’s method. On a uniform mesh of spacing *h =* (*rn+1 – rn*),

|  |  |  |
| --- | --- | --- |
|  |  |  |

Integration in the backward direction is symmetric with respect to the indices:

|  |  |  |
| --- | --- | --- |
|  |  |  |

If the interpoint spacing is non-uniform such that

|  |  |  |
| --- | --- | --- |
|  |  |  |

Equation (19) reduces to Eq(17) when *a* = *b*. Integration in the backward direction is *not* symmetric with respect to the indices:

|  |  |  |
| --- | --- | --- |
|  |  |  |

I’m not sure the non-uniform spacing equation is right – you’d think it should be symmetric with respect to interchange of a and b, but it is not – the primary issue are the + (*a*2 + *ab* – *b*2) and the – (*a*2 – *ab* – *b*2) terms – both of these just happen to reduce to + *h*2 when *a* = *b* = *h* and so give the proper limit, but they are not symmetric with respect to interchange of *a* and *b*.

# Rydberg Units

The Rydberg

The Bohr radius

Calculating muffin-tin potentials:

<http://hermes.phys.uwm.edu/projects/elecstruct/mufpot/MufPot.TOC.html>