Computer Lab: Numerical Solution to the Radial Schrödinger Equation

Part II: Many-electron Systems

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1 Introduction

We solve the time-independent Schrödinger equation for many-electron atoms using the *central-field approximation*, described in Sec. 2. In this approximation, each electron is assumed to move independently in a central average potential that accounts for the nuclear field and the field of the remaining electrons. The single-electron Schrödinger equation is then used to describe the electronic states of a many-electron atom. The concepts of the electron configuration and configuration energy are discussed in Sec. 3. There are various methods for determining approximate central average potentials. In this lab, we explore the simple *parametric potentials* (see Sec. 4). This potential is used in an example to compute configuration energies in neutral sodium (see Appendix A). In the exercises that you are asked to solve, many-electron systems other than sodium are investigated.

2 Central-field Approximation

For N-electron systems, the exact forms of the solutions to the Schrödinger equation are not known. Instead, approximate solutions must be found. One possibility that provides a lot of insight into the nature of the approximate solutions is to replace the non-relativistic Hamiltonian H with one for which the Schrödinger equation is solvable.

In the *central-field approximation*, the Hamiltonian H is replaced with the separable Hamiltonian H_0

$$H_0 = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + V(r_i) \right), \tag{1}$$

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where $V(r)$ is a central potential. The potential experienced by a bound atomic electron near $r = 0$ is dominated by the nuclear Coulomb potential and so, we expect

$$\lim_{r \to 0} V(r) \approx -\frac{Z}{r} \tag{2}$$

for small r. On the other hand, at large r, an electron experiences a potential that is the sum of the attractive nuclear Coulomb potential and the repulsive potential of the remaining electrons (the screening). Thus, we expect

$$\lim_{r \to \infty} V(r) = -\frac{\zeta}{r}, \tag{3}$$

with $\zeta = Z - N + 1$ for an N-electron atom with nuclear charge Z. This limiting form is referred to as the ionic potential. It is straightforward to devise a potential $V(r)$, depending on several adjustable parameters, that accounts for screening and interpolates between the inner nuclear potential and outer ionic potential. We will come back to this in Sec. 4.

Since H_0 is separable, the equation

$$H_0 \psi_0(\mathbf{q}_1, ..., \mathbf{q}_N) = E_0 \psi_0(\mathbf{q}_1, ..., \mathbf{q}_N) \tag{4}$$

is easy to solve. The eigenvalues and eigenfunctions can be written as

$$E_0 = \sum_{i=1}^{N} E_i \tag{5}$$

and

$$\psi_0(\mathbf{q}_1, ..., \mathbf{q}_N) = \prod_{i=1}^{N} \phi(\alpha_i; \mathbf{q}_i), \tag{6}$$

where the individual *spin-orbitals* are solutions to the one-electron equation

$$\left[-\frac{1}{2} \nabla^2 + V(r) \right] \phi(\alpha; \mathbf{q}) = E \phi(\alpha; \mathbf{q}). \tag{7}$$

As previously shown, the one-electron function (*spin-orbital*) can be written as

$$\phi(\alpha; \mathbf{q}) = \frac{1}{r} P_{n\ell}(r) Y_{\ell m_\ell}(\theta, \varphi) \chi_{m_s}(\sigma), \tag{8}$$

where the solutions are characterized by the quantum numbers $\alpha = n\ell m_\ell m_s$.

The Hamiltonian H_0 is invariant with respect to permutations of the electron coordinates, so that any permutation of the coordinates in the product function also leads to an eigenfunction. By combining the permuted product functions, we can form an antisymmetric function

$$\Phi(\mathbf{q}_1, ..., \mathbf{q}_N) = \mathcal{A} \prod_{i=1}^{N} \phi(\alpha_i; \mathbf{q}_i). \tag{9}$$

This function can also be represented as a so-called *Slater determinant*

$$\Phi(\mathbf{q}_1, ..., \mathbf{q}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi(\alpha_1; \mathbf{q}_1) & \phi(\alpha_1; \mathbf{q}_2) & ... & \phi(\alpha_1; \mathbf{q}_N) \\ \phi(\alpha_2; \mathbf{q}_1) & \phi(\alpha_2; \mathbf{q}_2) & ... & \phi(\alpha_2; \mathbf{q}_N) \\ \vdots & \vdots & & \vdots \\ \phi(\alpha_N; \mathbf{q}_1) & \phi(\alpha_N; \mathbf{q}_2) & ... & \phi(\alpha_N; \mathbf{q}_N) \end{vmatrix}. \tag{10}$$

In this representation, it is seen that the total wave function $\Phi(\mathbf{q}_1, ..., \mathbf{q}_N)$ vanishes identically if two electrons have the same value of the four quantum numbers $\alpha = n\ell m_\ell m_s$. Thus, for allowed states of the atom, no two electrons can have the same value of the four quantum numbers. This is the *exclusion principle* in the form originally discovered by Pauli (1925). Note also that the determinant vanishes whenever $\mathbf{q}_i = \mathbf{q}_j$; that is, whenever two electrons with the same spin have the same space coordinates.

To determine the parity of the *Slater determinant*, we use that each of the *spin-orbitals* building the *Slater determinant* has parity $(-1)^\ell$. The *Slater determinant* itself must therefore have the well-defined parity

$$\pi = (-1)^{\ell_1}(-1)^{\ell_2}...(-1)^{\ell_N} = (-1)^{\sum_{i=1}^N \ell_i}, \tag{11}$$

which is even, or odd, depending on whether the sum of the orbital angular momentum quantum numbers is even, or odd.

3 Electron Configuration

As seen above, an eigenfunction of the central-field Hamiltonian H_0 can be written as a *Slater determinant*. The corresponding energy E_0 is then given by the sum of the energies of the *spin-orbitals* appearing in the determinant, so that

$$E_0 = \sum_{i=1}^N E_i. \tag{12}$$

Spin-orbitals with the same values of the n and ℓ quantum numbers are said to belong to the same *subshell* (or shell, for short) and are called equivalent *spin-orbitals*. Correspondingly, we may loosely speak of electrons belonging to the same subshell and refer to them as *equivalent electrons*. Since the energy of a *spin-orbital* depends only on the n and ℓ quantum numbers, the energy E_0 is entirely determined by the *electron configuration*, that is the distribution of *spin-orbitals* with respect to the subshells. A general electron configuration is given by

$$(n_1\ell_1)^{w_1}(n_2\ell_2)^{w_2}...(n_m\ell_m)^{w_m}, \qquad N = \sum_{a=1}^m w_a, \tag{13}$$

where $w_1, w_2, ..., w_m$ are the occupation numbers of the *spin-orbitals* in the different subshells, m is the total number of occupied subshells. The corresponding energy can then be written as

$$E_0 = \sum_{a=1}^{m} w_a E_{n_a \ell_a}, \tag{14}$$

where $E_{n\ell}$ denotes the energy of the *spin-orbitals* in an $n\ell$ subshell. Often, the electron configurations are denoted by means of the spectroscopic symbols. For instance, $1s^2 2s^2 2p^2$ means that there are two electrons in each of the $1s$, $2s$, and $2p$ subshells.
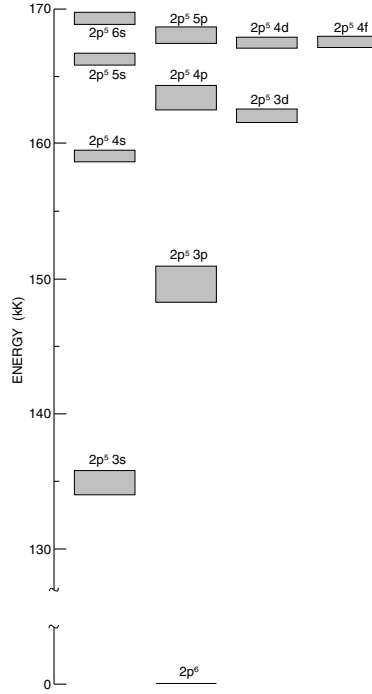

Figure 1: *Schematic diagram of the lowest configurations of Ne I. The levels of each configuration lie within the limited energy range shown by the shaded block.*

According to the Pauli *exclusion principle*, there can be only one electron in each *spin-orbital*, and thus there can be at most $2(2\ell+1)$ electrons in a subshell $n\ell$. A subshell which is fully occupied is said to be *closed* in contrast to a partially occupied shell which is said to be *open*. According to Eq. (14), the energy of a configuration is given by the occupation numbers of each subshell. Therefore, the ground configuration for a particular atom should be obtained by successively filling the electron subshells with the lowest energies $E_{n\ell}$ leading to a number of closed subshells and at most one open shell. This is what is known as the "auf Bau" principle formulated by Bohr (1922) to explain the periodic table of the elements.

The concept of a configuration has a simple interpretation. For light atoms, the experimental energy levels often appear in closely spaced groups, as shown in Fig. 1. When a *central-field* calculation is performed using a suitable central potential $V(r)$, it is found that the average energy of each of these groups matches well with the energy of a certain configuration and thus, it is possible to assign configuration labels to the groups. Furthermore, if the assignment of the configuration has been done correctly, it is seen that the number of states [3] in a group is equal to the number of determinants of the corresponding configuration.

4 Parametric Potentials

Different central potentials have been used in atomic structure calculations. Here, we look at a rather simple one, given by

$$V_a(r) = -\frac{Z}{r} + \frac{(Z-\zeta)r}{a^2+r^2}, \tag{15}$$

which depends on one parameter a. The parameter is adjusted so that the computed energies in the *central-field approximation* agree as close as possible with the experimental energies. Analyzing the potential, we see that it indeed assumes the limiting values of Eqs. (2) and (3), just as it should. As an example, we look at neutral sodium (Na I) with $Z = 11$ and $N = 11$ (that is $\zeta = 1$). In Fig. 2, the second part of the effective potential, i.e., the part related to the repulsive potentials of the remaining electrons, is displayed for $a = 0.2683$, which is a value that has been shown to give a good agreement between the computed energy levels and the observed ones.
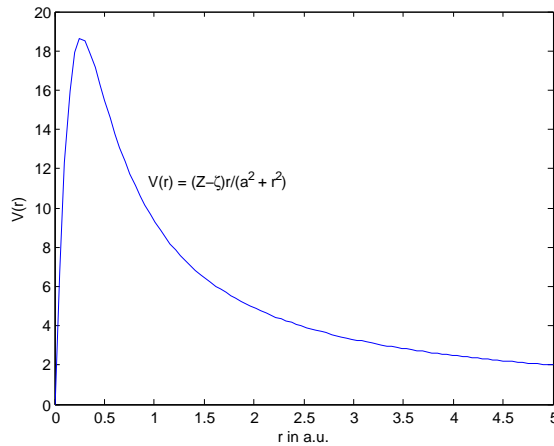

Figure 2: *Second part of the effective potential, that is the part related to the repulsive potentials of the remaining electrons.*

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[3]The number of states belonging to a degenerate level can be inferred experimentally by placing the atom in an external magnetic field, where the degeneracy with respect to the M quantum numbers is removed.

5   References

Part of the material can be found in C. Froese Fischer, T. Brage, and P. Jönsson, Computational Atomic Structure, IoP, Bristol (ISBN 0-7503-0466-9)

The interested reader should consult R. Cowan, The Theory of Atomic Structure and Spectra, Univ. of California Press, Berkely (ISBN 0-520-03821-5)

6   Preparatory question

Before the lab, read the lab manual and answer this preparatory question. The following numbered questions in this and the second part of the lab should be answered in the report.

5. Describe in words what the Slater determinant representation of the wave function is and how, using the mathematical properties of the determinant, we can see that the Slater determinant takes into account both the antisymmetry property of the wave function as well as the Pauli exclusion principle.

7   Exercises

Modify the program `radiallog.py` so that it uses the parametric potential $V_a(r) = -\frac{Z}{r} + \frac{(Z-\zeta)r}{a^2+r^2}$ instead of the Coulomb potential. In order to do this, you must both modify the effective potential $U = V(r) + \frac{\ell(\ell+1)}{2r^2}$ and the g function for Numerov (*see* the description of the Cowell-Numerov's method in the manual for part 1 of the lab).

6. Perform calculations for Na I, (for this system $a = 0.2683$). Calculate configuration energies and verify that the values given in Appendix A.1 are correct, make a table containing the computed energy values. Plot some of the radial functions in a single plot. Look at the energies for Na I in NIST and note in which order the configurations come. Look up Al III and compare. Is the order of the configurations different, why could this be the case? Note that in NIST you can choose to have the energies printed in Hartrees, which are the same units that the program uses, i.e. atomic units.

7. Perform calculations for Li I, $Z = 3$ and $N = 3$. Modify the value of the a parameter so that your energy differences fit those reported in the NIST database. How do the energies change when we change the a parameter? Do some additional programming to automate this testing. This can be done by for example using this command which minimizes a function with respect to the variable.

```
import scipy.optimize as opt
def residuals(variable):
    return (difference between the value to be optimized and the goal value)
optimized_variable, error = opt.leastsq(residuals, variable_first_guess)
```

opt.leastsq varies the variable to make residuals give as small a value as possible. Note that a first guess must be given to the function. Create tables containing the configuration, the computed value and the NIST value. Plot some wave functions in a single plot.

A Sodium example

A.1 Sodium Energy Levels

As an example, we will look at the energies in Na I. The ground configuration is $1s^2 2s^2 2p^6 3s$ and the excited configurations are given by $1s^2 2s^2 2p^6 3p$, $1s^2 2s^2 2p^6 3d$, etc. We modify the Python program `radiallog.py` to handle the parametric potential given by Eq. (15) with $a = 0.2683$. Using the program we obtain the following energies:

orbital	energy in a.u.
$1s$	-47.4653
$2s$	-1.6452
$2p$	-0.5532
$3s$	-0.1919
$3p$	-0.1072
$3d$	-0.0571
$4s$	-0.0720
$4p$	-0.0494
$4d$	-0.0321
$4f$	-0.0315
$5s$	-0.0377

From the energies above, we can compute the energies of the configurations. For the ground configuration $1s^2 2s^2 2p^6 3s$, we have

$$E(2p^6 3s) = 2E_{1s} + 2E_{2s} + 6E_{2p} + E_{3s}\,. \tag{16}$$

The energy of the first excited configuration $1s^2 2s^2 2p^6 3p$ is given by

$$E(2p^6 3p) = 2E_{1s} + 2E_{2s} + 6E_{2p} + E_{3p}\,. \tag{17}$$

Normally, the energies of a configuration are not observable. What can be observed is the energy differences between different configurations. Thus, spectroscopic tables, such as the ones from NIST `physics.nist.gov/PhysRefData/ASD/` `levels_form.html`, give the energy differences between the excited states and the ground state. These differences should be compared with theory. Below, we show an excerpt from the spectroscopic table for Na I. Energies are given in cm^{-1}, where 1 a.u. corresponds to $219\,474.63$ cm^{-1}.

```
------------------------------------------------|
Configuration  | Term |   J  |       Level      |
---------------|------|------|----------------|
               |      |      |                  |
2p6.3s         | 2S   | 1/2  |       0.00000    |
               |      |      |                  |
2p6.3p         | 2P*  | 1/2  |   16956.17025    |
               |      | 3/2  |   16973.36619    |
               |      |      |                  |
```

```
2p6.4s          | 2S    | 1/2 |   25739.999       |
                |       |     |                   |
2p6.3d          | 2D    | 5/2 |   29172.837       |
                |       | 3/2 |   29172.887       |
                |       |     |                   |
2p6.4p          | 2P*   | 1/2 |   30266.99        |
                |       | 3/2 |   30272.58        |
                |       |     |                   |
2p6.5s          | 2S    | 1/2 |   33200.673       |
                |       |     |                   |
2p6.4d          | 2D    | 5/2 |   34548.729       |
                |       | 3/2 |   34548.764       |
                |       |     |                   |
2p6.4f          | 2F*   | 7/2 |   34586.92        |
                |       | 5/2 |   34586.92        |
----------------------------------------------------|
```

Inserting the energies for the *spin-orbitals* and taking the energy differences, our simple model with the parametric potential gives the following values:

```
------------------------------------------------------------|
Configuration  | Term |  J  |  Level (NIST)   |  Calc.   |
---------------|------|-----|-----------------|----------|
               |      |     |                 |          |
2p6.3s         | 2S   | 1/2 |      0.00000    |          |
               |      |     |                 |          |
2p6.3p         | 2P*  | 1/2 |   16956.17025   |   18589  |
               |      | 3/2 |   16973.36619   |          |
               |      |     |                 |          |
2p6.4s         | 2S   | 1/2 |   25739.999     |   26315  |
               |      |     |                 |          |
2p6.3d         | 2D   | 5/2 |   29172.837     |   29585  |
               |      | 3/2 |   29172.887     |          |
               |      |     |                 |          |
2p6.4p         | 2P*  | 1/2 |   30266.99      |   31275  |
               |      | 3/2 |   30272.58      |          |
               |      |     |                 |          |
2p6.5s         | 2S   | 1/2 |   33200.673     |   33843  |
               |      |     |                 |          |
2p6.4d         | 2D   | 5/2 |   34548.729     |   35072  |
               |      | 3/2 |   34548.764     |          |
               |      |     |                 |          |
2p6.4f         | 2F*  | 7/2 |   34586.92      |   35204  |
               |      | 5/2 |   34586.92      |          |
------------------------------------------------------------|
```

We see that the consistency is quite good and that our model indeed gives the correct order of the configurations. We also note that, in this atomic system,

the energies depend quite strongly on the orbital quantum numbers so that, e.g., $2p^6 4s$ lies below $2p^6 3d$. For highly charged ions, energies are usually ordered by the principal quantum number n.

A.2   Sodium Radial Orbitals

In Fig. 3, we present the radial functions (or radial orbitals) as predicted by our model. The radial orbital for $1s$ is strongly contracted and has a peak at around $r = 0.1$. Comparing the radial orbitals for $2s$ and $2p$, we see that the electron corresponding to $2s$ has some probability to be found close to the nucleus, where it sees a more unscreened nuclear charge. As a result, the energy of $2s$ will be lower than the energy of the $2p$. The same arguments can be used to see why the energy of $3s$ is lower than the ones of the $3p$ and $3d$.
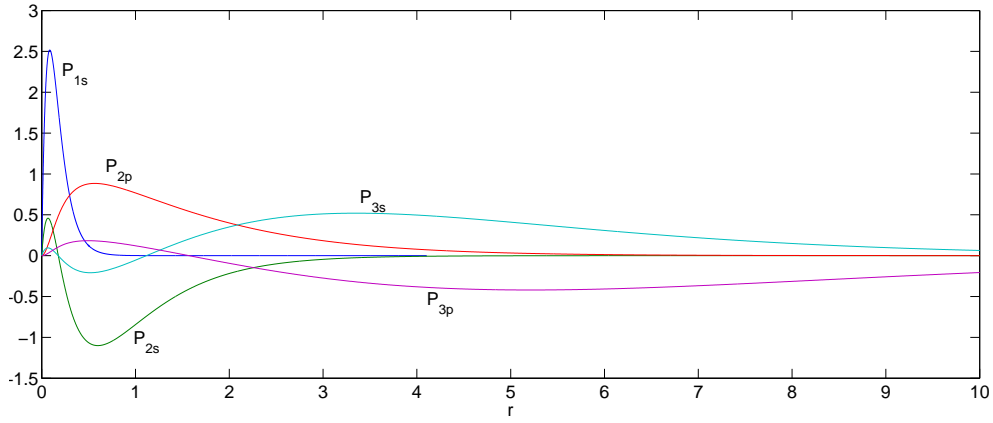

Figure 3: *Radial orbitals in Na I from calculations using a parametric potential.*