Using one electron two center Coulomb solutions together with Bohr-like methods

I. SOLUTION OF TWO CENTER COULOMB PROBLEM

For a given separation distance R and a magnetic quantum number m, energy levels of one electron in a field of two charges, $Z_1 = 1$ and $Z_2 = qZ_1$, could be determined by solving a system of two polynomial equations[1],

$$\det(\mathsf{F} - a\mathsf{I}) = 0, \tag{1}$$

$$\det(\mathsf{G} + a\mathsf{I}) = 0 \tag{2}$$

in respect to two unknown variables, a and p. Nonzero matrix elements of F and G are defined as

$$\begin{aligned}
F_{j,j} &= -(m+j)(m+j+1) + \frac{p^2}{(2m+2j+1)}\left[\frac{j(2m+j)}{2m+2j-1} + \frac{(j+1)(2m+j+1)}{2m+2j+3}\right], \\
F_{j,j+1} &= R(q-1)\frac{2m+j+1}{2m+2j+3}, \\
F_{j,j-1} &= R(q-1)\frac{j}{2m+2j-1}, \\
F_{j,j+2} &= p^2\frac{(2m+j+2)(2m+j+1)}{(2m+2j+5)(2m+2j+3)}, \\
F_{j,j-2} &= p^2\frac{j(j-1)}{(2m+2j-3)(2m+2j-1)}, \\
G_{j,j} &= 2j(s-2p-j) + m(m+s+1) + s(1+2p) - p^2, \\
G_{j,j+1} &= (j+1)(j+1+m), \\
G_{j,j-1} &= (j-1-s)(j-1-s-m), \quad 0 \le j \le j_{\max}
\end{aligned}$$

Only solutions with real and positive p of equations (1) and (2) are selected. Finally, the energy is determined as

$$E = -2\frac{p^2}{R^2}. \tag{3}$$

II. EXAMPLE: $m = 0$ MANIFOLD OF H_2^+

Size of matrixes $j_{\max}$ is sufficient to determine energy levels with accuracy $\sim 10^{-10}$. First 55 calculated levels are shown in Fig. 1.

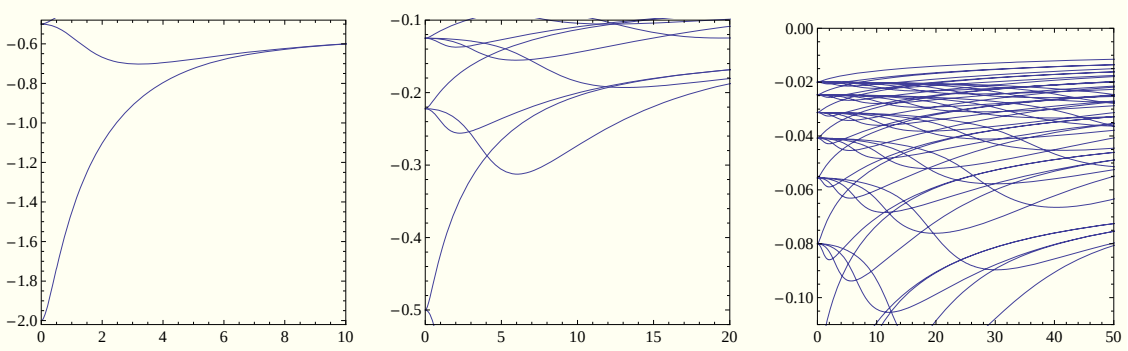

FIG. 1. $m = 0$ manifold of electronic energy levels of H_2^+. Left panel - ground and first excited states, middle panel - third and higher excited states up to 9-th, right panel - 10th and higher excited states up to 55-th.

III. CALCULATION OF ENERGY OF LiH MOLECULE USING A CONSTRAINT FOR THE CORRESPONDING ION

As an example of utilizing of ionic energy in Bohr model, we calculate the energy of LiH. In this molecule, $n = 2$ electron of Lithium atom is situated much farther from other three electrons, that form a core resembling a LiH^+ ion. Therefore, we used a constraint

$$W_{\text{ion}} = E_{\text{ion}}(R), \tag{4}$$

where W_{ion} is Bohr ionic energy, and E_{ion} is exact ionic energy. Results are shown in Fig. 2.

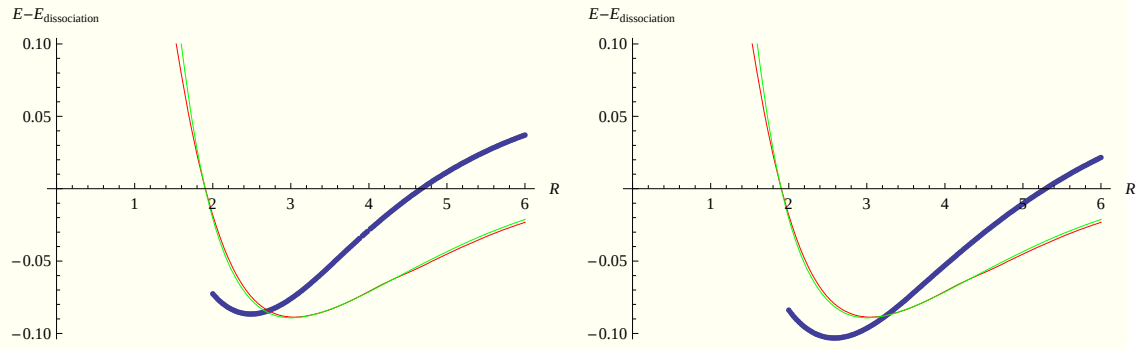

FIG. 2. Energy of the molecule LiH as a function of separation distance R. Fine lines - exact quantum calculations from two different sources, thick line - Bohr model with ionic constraint (4). Left panel - using Heitler-London constraint for two active electrons, right panel - Hund-Mulliken constraint

IV. CALCULATION OF ENERGY OF LiH^+ ION USING AN ONE-ELECTRON TWO CENTER MODEL WITH EFFECTIVE CHARGES

The energy of LiH^+ ion is modelled by an excited state of H_2^+-like molecule with effective charges. It is necessary to correct the charges because without the correction the energy has no minimum. Notice that since the outer electron of Li has radius 2.83 (according to Slater[2]), but not 4. It means that there is no complete shielding of nuclear charge by inner electrons. Radius of orbit is n^2/Z_{eff}^2. From this equation, we could determine the effective charge as $\sqrt{4/r} = 1.19$. The energy of a one-electron molecule with charges $Z_1 = 1.33$ and $Z_2 = 1$ is plotted on Fig. 3. It is quite close to the energy of LiH^+.

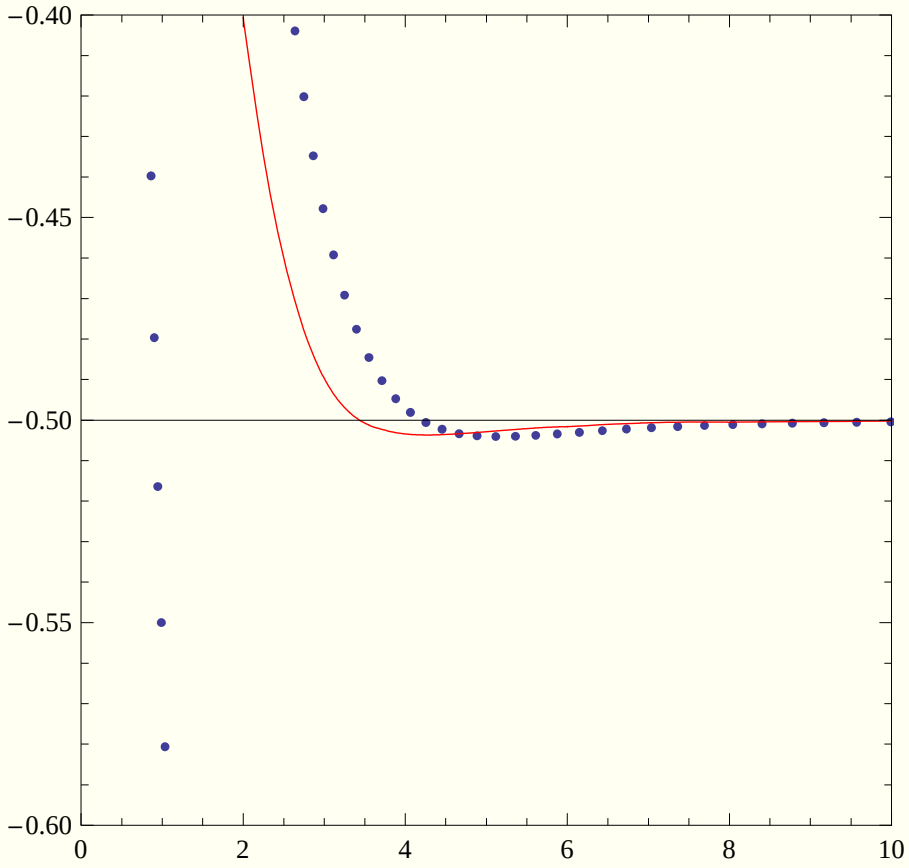

FIG. 3. Energy of the molecule LiH^+ (red line) and corresponding effective charge one-electron model (dotted line) (the figure should be slightly corrected because it was done for $Z_1 = 1.33$ instead of correct $Z_1 = 1.119$)

[1] Q. Chi, S. Kais, F. Remacle, R. D. Levin. J. Chem. Phys, **114**, 9697, 2001.

[2] J. Slater, Quantum Theory of Atomic Structure, vol. 1, p. 210.