# Problems Chapter 10

Quantum Mechanics
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## Problem 1

*Apply a variational method with hydrogenoid wave functions to the computation of the ground state energy of the helium. Use Temple's method to give an estimate of the error.*

### Solution

The variational wave function is (see also the text)

$$\psi[\mathbf{x}_1, \mathbf{x}_2] = \varphi[r_1]\,\varphi[r_2]; \qquad \varphi[r] = \frac{1}{\sqrt{\pi}} Z_1^{3/2}\, e^{-Z_1 r}\,. \tag{1.1}$$

We use atomic units. $Z_1$is the variational parameter and plays the role of an effective charge.

The Hamiltonian of the system is

$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \equiv H_0 + H_{12}\,. \tag{1.2}$$

In the text it has been shown that

$$\langle \psi \,|\, H \,|\, \psi \rangle = -\left(Z - \frac{5}{16}\right)^2. \tag{1.3}$$

which has a minimum at

$$Z_1 = Z - \frac{5}{16}. \tag{1.4}$$

The Temple estimate for the error is

$$\mathcal{E} - \sqrt{\sigma} \le E \le \mathcal{E} + \sqrt{\sigma}\,, \tag{1.5}$$

where $\mathcal{E}$ is the exact value and $\sigma$ is the variance of the variational calculation

$$\sigma = \langle H\psi \,\big|\, H\psi \rangle - E^2 = \langle H_0\psi \,\big|\, H_0\psi \rangle + 2\langle H_0\psi \,\big|\, H_{12}\psi \rangle + \langle H_{12}\psi \,\big|\, H_{12}\psi \rangle - E^2. \tag{1.6}$$

In polar coordinates we have easily

$$H_0\,\psi = \left(-Z_1^2 + (Z_1 - Z)\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\right)\psi; \qquad H_{12}\,\psi = \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}\,\psi. \tag{1.7}$$

From (1) it follows easily

$$\langle \psi \,|\, \frac{1}{r_1} \,|\, \psi \rangle = Z_1\,; \quad \langle \psi \,|\, \frac{1}{r_1^2} \,|\, \psi \rangle = 2\,Z_1^2\,;$$

substitution in previous equation gives

$$\langle H_0\psi \,|\, H_0\psi \rangle = Z_1^2\left(6\,Z^2 - 8\,Z\,Z_1 + 3\,Z_1^2\right). \tag{1.8}$$

The second term in (6) is, using again (7) and symmetry

$$\langle H_0\psi \,|\, H_{12}\psi \rangle = -Z_1^2\,\langle \psi \,\Big|\, H_{12} \,|\, \psi \rangle + 2\,(Z_1 - Z)\int \psi\,\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}\,\frac{1}{r_1}\,\psi = -\frac{5}{8}Z_1^3 + 2\,(Z_1 - Z)\,I.$$

Use has been made of the integral computed in the text

$$\langle\, \psi \mid H_{12} \mid \psi \,\rangle = \frac{5}{8} Z_1. \tag{1.9}$$

The integral I can be computed using multipole expansion (or using Fourier transform):

$$\frac{1}{\mid \mathbf{r}_1 - \mathbf{r}_2 \mid} = \sum_{\ell=0}^{\infty} \frac{1}{r_>} \left(\frac{r_<}{r_>}\right)^{\ell} P_\ell[\mathrm{Cos}\,(\gamma)]; \tag{1.10}$$

Only the term with $\ell = 0$ contributes

$$I = (4\,\pi)^2 \left(\int_0^{\infty} dr_1\, r_1^2 \int_0^{r_1} dr_2\, r_2^2 \frac{1}{r_1^2} (\varphi[r_1]\, \varphi[r_2])^2 + \int_0^{\infty} dr_1\, r_1^2 \int_0^{r_1} dr_2\, r_2^2 \frac{1}{r_1} \frac{1}{r_2} (\varphi[r_1]\, \varphi[r_2])^2\right) = \frac{3}{4} Z_1^2.$$

The third integral in (6) can be written, rescaling coordinates with $r \to x / Z_1$:

$$\langle\, H_{12}\, \psi \mid H_{12}\, \psi \,\rangle = \frac{Z_1^2}{\pi^2} \int d^3 x_1\, d^3 x_2 \frac{1}{\mid \mathbf{x}_1 - \mathbf{x}_2 \mid^2} e^{-2\, x_1}\, e^{-2\, x_2}.$$

Taking the z axis along the direction of $x_1$, the integrand depend only on $\theta$, the angle between $x_1$and $x_2$. Integrating on the rest of angles give a facto $4\pi$ for the solid angle of $x_1$and a factor $2\pi$ for the azimuthal angle of $x_2$, then

$$\langle\, H_{12}\, \psi \mid H_{12}\, \psi \,\rangle = \frac{Z_1^2}{\pi^2} 8\, \pi^2 \int dr_1\, r_1^2\, dr_2\, r_2^2\, d\, (\mathrm{Cos}[\theta]) \frac{1}{r_1^2 + r_2^2 - 2\, r_1\, r_2\, \mathrm{Cos}[\theta]} e^{-2\,(r_1 + r_2)} = \frac{2}{3} Z_1^2.$$

The integral in $\theta$ is elementary. The radial integral can be computed integrating by part. The whole integral an also been computed using Fourier transform, with the three dimensional transforms:

$$\mathcal{F}[e^{-r}] = \frac{8\,\pi}{\left(\mathbf{k}^2 + 1\right)^2}; \quad \mathcal{F}\left[\frac{1}{r^2}\right] = \frac{2\,\pi^2}{\mid \mathbf{k} \mid}.$$

Summing the various contribution we get, inserting the value for $Z_1$and with Z=2

$$\sigma = \frac{121\,(5 - 16\,Z)^2}{98\,304} \simeq 0.897; \quad \sqrt{\sigma} \simeq 0.95\,.$$

As the first order value is E~2.85 we see that Temple's estimate is quite poor.

# Problem 2

*Let us interpret the scale parameter $\alpha$ used in the variational computations of anharmonic oscillator as a variable frequency. Show that the choice used in the test is the one suggested by the Bohr-Sommerfeld quantization conditions.*

## Solution

### The choice of the scale

The Hamiltonian of the problem is

$$H = \frac{1}{2} p^2 + \frac{\mu}{2} x^2 + \frac{g}{2} x^4. \tag{2.1}$$

In the text and in the numerical applications we introduced a scale parameter $\alpha$ with the change of variables $x \to x/\alpha$:

$$H_\alpha = \frac{1}{2} \alpha^2\, p^2 + \frac{\mu}{2\,\alpha^2} x^2 + \frac{g}{2\,\alpha^4} x^4. \tag{2.2}$$

Clearly the spectrum do not depend on a change of variables, or, equivalently, $dE[\alpha]/d\alpha = 0$, the eigenvalues are stationary with respect to $\alpha$ variations. This is true in the exact problem. If the problem is solved with within a finite - size basis Hilbert space, the stationarity with respect to $\alpha$ becomes a constraint which select the "best" approximation.

In the text we try to make this choice of $\alpha$ nearly independent on the particular eigenvalue to be studied, by minimizing the mean value of H on the highest state in the basis. The idea is that lower eigenvalues for systems like an anharmonic oscillator are more stable, than a stabilization of high eigenvalues automatically should work for the lower ones.

Let $f_k[x]$ the usual harmonic oscillator basis with $\omega$=1:

$$f_k[x] = \frac{1}{\pi^{1/4}} \frac{1}{\sqrt{2^{k-1}\,(k-1)\,!}} H_{k-1}[x]\,\mathrm{Exp}[-x^\wedge 2/2];\quad k = 1,\,2,\,\ldots \tag{2.3}$$

The scale parameter $\alpha$ is introduced by taking as a basis the functions

$$F_k[x] = \sqrt{\alpha}\; f_k[\alpha\, x]. \tag{2.4}$$

A change of scale show that matrix elements of the Hamiltonian (1) in this basis are equal to matrix element of the modified Hamiltonian in the basis $f_k$:

$$\int dx\, F_k[x]\, H[x]\, F_j[x] = \alpha \int dx\, f_k[\alpha\, x]\, H[x]\, f_j[\alpha\, x] = \int dy\, f_k[y]\, H\left[\frac{y}{\alpha}\right] f_j[y] = \int dy\, f_k[y]\, H_\alpha[y]\, f_j[y]. \tag{2.5}$$

The wave functions of an harmonic oscillator depend on x through the combination

$$\xi^2 = m\,\omega\, x^2$$

then the functions $F_k$ can be viewed as the harmonic oscillator functions for an oscillator with $\omega = \alpha^2$.

In this interpretation the best $\alpha$ is the best frequency to choose for the basis functions. The problem of optimization for $\alpha$ can be stated in the alternative way: which is the best oscillator which approximate the system? If we found this oscillator we expect that the zero order approach to the problem is optimal.

- **The equation for $\alpha$**

From known matrix elements for x and p it is trivial to compute the mean value of the Hamiltonian for the n-th state of the $\alpha$ oscillator.

From

$$\begin{aligned} &< n \mid x^2 \mid n > = \frac{\hbar}{m\omega}\frac{2\,n+1}{2}; \\ &< n \mid x^4 \mid n > = \left(\frac{\hbar}{m\omega}\right)^2 \frac{3}{4}\left(2\,n^2+2\,n+1\right); \\ &< n \mid p^2 \mid n > = \hbar\, m\,\omega\, \frac{2\,n+1}{2}; \end{aligned} \tag{2.6}$$

we have (we write $\omega = \alpha^2$ )

$$E[\omega] = \langle n \mid H_\alpha \mid n\rangle = \frac{2\,n+1}{4}\left(\omega + \frac{\mu^2}{\omega}\right) + \frac{3}{8}\, g\, \frac{1}{\omega^2}\left(2\,n^2+2\,n+1\right). \tag{2.7}$$

Stationarity with respect to $\omega$, i.e. imposing $\partial E/\partial\omega = 0$, we get

$$\mu^2\,(2\,n+1)\,\omega - \omega^3\,(2\,n+1) + 3\,g\left(1+2\,n+2\,n^2\right) = 0. \tag{2.8}$$

With $\omega \to \alpha^2$this is the equation used in the text and in the numerical notebooks.

- **Bohr Sommerfeld conditions**

For large n we see that to cancel the quadratic term in (8) $\omega$ must grow with n. The leading term in n becomes

$$-\omega^3\,2\,n + 6\,g\,n^2 = 0 \;\Rightarrow\; \omega \sim (3\,g\,n)^{1/3}.$$

Substitution in (7) gives at the leading order in n

$$E \sim \frac{3}{4}(3\,g)^{1/3}\, n^{4/3} \simeq 1.08\, g^{1/3}\, n^{4/3}. \tag{2.9}$$

To (9) contribute the kinetic term and the anharmonic term, in agreement with the expectation that for high energies the $x^4$term is the leading term in potential energy.
At large n we expect that old quantum theory is at work. The Bohr Sommerfeld quantization condition

$$2\int_a^a dx\,\sqrt{2\,E - \mu^2\,x^2 - g\,x^4} = 2\,\pi\,n,$$

with $\pm a$ the classical inversion points, should give a good approximation to the eigenvalues of (1). For large n we can neglect the $x^2$term, the inversion points are approximated by

$$\pm a = \pm \left(\frac{2\,E}{g}\right)^{1/4},$$

and the Bohr Sommerfeld condition reads, with x = a z:

$$2\,\pi\,n = 2\left(\frac{2\,E}{g}\right)^{1/4}\sqrt{2\,E}\int_{-1}^{1} dz\,\sqrt{1-z^4} = 2^{7/4}\,g^{-1/4}\,E^{3/4}\,K\,;$$

$$K = \frac{\sqrt{\pi}\,\Gamma[1/4]}{4\,\Gamma[7/4]} \simeq 1.748$$

The resulting energies are

$$E \sim 2^{-7/3}\left(\frac{2\,\pi}{K}\right)^{4/3} g^{1/3}\,n^{4/3} \simeq 1.09\,g^{1/3}\,n^{4/3}. \qquad (2.10)$$

Confronting this result with (9) we see that our choice for $\omega$ (i.e. for $\alpha$) gives an almost correct result for higher n, this means that our effective oscillator, by itself, fit the levels. In terms of the Hamiltonian matrix the diagonal elements of the $H_\alpha$ Hamiltonian give almost the whole eigenvalue, the mixing with other states is small, this means that our approximation is a good one.

## Problem 3

*Compute the corrections m/M to the helium atom Hamiltonian by an explicit coordinate transformation in the Schrödinger equation.*

### Solution

The Hamiltonian of the problem is:

$$H = \frac{1}{2\,m}\,\mathbf{q}_1^2 + \frac{1}{2\,m}\,\mathbf{q}_2^2 + \frac{1}{2\,M}\,\mathbf{q}_N^2 - \frac{Z\,e^2}{|\,\boldsymbol{\xi}_1 - \boldsymbol{\xi}_N\,|} - \frac{Z\,e^2}{|\,\boldsymbol{\xi}_2 - \boldsymbol{\xi}_N\,|} + \frac{e^2}{|\,\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2\,|} \qquad (3.1)$$

$\boldsymbol{\xi} = (\xi, \eta, \zeta)$ are the coordinates of the electron (1,2) and of the nucleus in a given inertial frame. **q** are the momenta in the inertial frame.

We change coordinates choosing as independent degrees of freedom the coordinates of center of mass of the system and the *relative* coordinate of the electrons with respect to the nucleus:

$$\mathbf{X} = \frac{1}{2\,m + M}\left(M\,\boldsymbol{\xi}_N + m\,\boldsymbol{\xi}_1 + m\,\boldsymbol{\xi}_2\right)\;; \quad \mathbf{x}_1 = \boldsymbol{\xi}_1 - \boldsymbol{\xi}_N\;; \quad \mathbf{x}_2 = \boldsymbol{\xi}_2 - \boldsymbol{\xi}_N\,. \qquad (3.2)$$

The interaction depend only on x coordinates as $\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2 = \mathbf{x}_1 - \mathbf{x}_2$ .

Let us consider the change of variables for one axis, the first as an example (index here refer to electrons, i,j = 1,2 )

$$\frac{\partial}{\partial \xi_i} = \frac{\partial X}{\partial \xi_i}\,\frac{\partial}{\partial X} + \sum_{j=1}^{2} \frac{\partial x_j}{\partial \xi_i}\,\frac{\partial}{\partial x_j} = \frac{m}{2\,m + M}\,\frac{\partial}{\partial X} + \frac{\partial}{\partial x_i}\,;$$
$$\frac{\partial}{\partial \xi_N} = \frac{\partial X}{\partial \xi_N}\,\frac{\partial}{\partial X} + \sum_{j=1}^{2} \frac{\partial x_j}{\partial \xi_N}\,\frac{\partial}{\partial x_j} = \frac{M}{2\,m + M}\,\frac{\partial}{\partial X} - \frac{\partial}{\partial x_1} - \frac{\partial}{\partial x_2}\,; \qquad (3.3)$$

In the Schrödinger representation q = $-i\,\hbar\,\partial/\partial\xi$. Defining the corresponding momenta in the C.M. frame:

$$\mathbf{P} = \frac{\hbar}{i}\,\frac{\partial}{\partial \mathbf{X}}\;; \quad \mathbf{p}_i = \frac{\hbar}{i}\,\frac{\partial}{\partial \mathbf{x}_i} \qquad (3.4)$$

The relations (3) imply

$$\mathbf{q}_i = \frac{m}{2\,m + M}\,\mathbf{P} + \mathbf{p}_i\;; \quad \mathbf{q}_N = \frac{M}{2\,m + M}\,\mathbf{P} - (\mathbf{p}_1 + \mathbf{p}_2)\,. \qquad (3.5)$$

The two terms in kinetic energy become

$$\frac{1}{2\,M}\,\mathbf{q}_N^2 = \frac{1}{2}\,\frac{M}{(2\,m + M)^2}\,\mathbf{P}^2 - \frac{1}{2\,m + M}\,\mathbf{P}\cdot(\mathbf{p}_1 + \mathbf{p}_2) + \frac{1}{2\,M}\,(\mathbf{p}_1 + \mathbf{p}_2)^2;$$
$$\frac{1}{2\,m}\,\mathbf{q}_1^2 + \frac{1}{2\,m}\,\mathbf{q}_2^2 = \frac{m}{(2\,m + M)^2}\,\mathbf{P}^2 + \frac{1}{2\,m}\,\mathbf{p}_1^2 + \frac{1}{2\,m}\,\mathbf{p}_2^2 + \frac{1}{2\,m + M}\,\mathbf{P}\cdot(\mathbf{p}_1 + \mathbf{p}_2)\,. \qquad (3.6)$$

And summing the two contribution

$$E_{\mathrm{Kin}} = \frac{1}{2\,m+M}\,\mathbf{P}^2 + \frac{1}{2\,\mu}\left(\mathbf{p}_1^2 + \mathbf{p}_2^2\right) + \frac{1}{M}\,\mathbf{p}_1\cdot p_2\,; \qquad \mu = \frac{m\,M}{m+M} = \text{reduced mass of the electron.} \tag{3.7}$$

The total Hamiltonian takes the form

$$H = \frac{1}{2\,m+M}\,\mathbf{P}^2 + \left(\frac{1}{2\,\mu}\left(\mathbf{p}_1^2 + \mathbf{p}_2^2\right) + U\right) + \frac{1}{M}\,\mathbf{p}_1\cdot p_2\,. \tag{3.8}$$

The first term is the kinetic energy due to the movement of the center of mass of the atom. The second term is the one usually considered to compute energy levels: it is equivalent to a system with an infinite mass nucleus where electron mass has been substituted by the reduced mass. The last term is called mass correction, or polarization term.

## Problem 4

*Perform the change of variables for Hylleraas coordinates in helium*

$$s = r_1 + r_2\,;\; t = r_1 - r_2\,;\; u = r_{12}; \qquad 0 \le t \le u \le s \le \infty \tag{4.1}$$

*Write the Schrödinger equation for a rotational invariant state in these coordinates.*

### Solution

If (r, $\theta$, $\varphi$) the angular coordinates for each electron and $\gamma$ is the angle between the directions between the two vectors $\mathbf{x}_1$and $\mathbf{x}_2$:

$$r_{12}^2 = r_1^2 + r_2^2 - 2\,r_1\,r_2\,\mathrm{Cos}[\gamma]; \qquad \mathrm{Cos}[\gamma] = \mathrm{Cos}[\theta_1]\,\mathrm{Cos}[\theta_2] + \mathrm{Sin}[\theta_1]\,\mathrm{Sin}[\theta_2]\,\mathrm{Cos}[\varphi_2 - \varphi_1]\,.$$

From (1) and this relation one get easily the relations

$$\begin{aligned}
&r_1^2 + r_2^2 = \frac{s^2+t^2}{2}; \quad 2\,r_1\,r_2 = \frac{s^2-t^2}{2};\\
&\frac{1}{r_1} + \frac{1}{r_2} = \frac{r_1+r_2}{r_1\,r_2} = \frac{4\,s}{s^2-t^2}; \quad \frac{1}{r_1} - \frac{1}{r_2} = \frac{r_2-r_1}{r_1\,r_2} = -\frac{4\,t}{s^2-t^2};\\
&1 - \mathrm{Cos}[\gamma] = 2\,\frac{u^2-t^2}{s^2-t^2}; \quad 1 + \mathrm{Cos}[\gamma] = 2\,\frac{s^2-u^2}{s^2-t^2}\,.
\end{aligned} \tag{4.2}$$

A function with spherical symmetry can depend only on s, t, u variables. Let us see how the usual derivatives are written on $\psi$[s,t,u]. x and y are the coordinates of electron 1 and 2 respectively. A short computation gives

$$\begin{aligned}
&\frac{\partial}{\partial x^i}\,\psi = \frac{x^i}{r_1}\,\partial_s\psi + \frac{x^i}{r_1}\,\partial_t\psi + \frac{x^i - y^i}{r_{12}}\,\partial_u\psi\,;\\
&\frac{\partial}{\partial x^i}\left(\frac{x^i}{r_1}\,\partial_s\psi\right) = \frac{2}{r_1}\,\partial_s\psi + \partial_{ss}\psi + \partial_{st}\psi + \frac{\mathbf{x}\cdot(\mathbf{x}-\mathbf{y})}{r_1\,r_{12}}\,\partial_{su}\psi\,;\\
&\frac{\partial}{\partial x^i}\left(\frac{x^i}{r_1}\,\partial_t\psi\right) = \frac{2}{r_1}\,\partial_t\psi + \partial_{st}\psi + \partial_{tt}\psi + \frac{\mathbf{x}\cdot(\mathbf{x}-\mathbf{y})}{r_1\,r_{12}}\,\partial_{tu}\psi\,;\\
&\frac{\partial}{\partial x^i}\left(\frac{x^i - y^i}{r_{12}}\,\partial_u\psi\right) = \frac{2}{r_{12}}\,\partial_u\psi + \frac{\mathbf{x}\cdot(\mathbf{x}-\mathbf{y})}{r_1\,r_{12}}\left(\partial_{su}\psi + \partial_{tu}\psi\right) + \partial_{uu}\psi.
\end{aligned}$$

Using

$$\mathbf{x}\cdot(\mathbf{x}-\mathbf{y}) = \frac{1}{2}\,(\mathbf{x}+\mathbf{y})\cdot(\mathbf{x}-\mathbf{y}) + \frac{1}{2}\,(\mathbf{x}-\mathbf{y})^2 = \frac{s\,t + u^2}{2};$$

one can compute easily the action of the laplacian operator for the first variable on $\psi$

$$\Delta_x\,\psi = \frac{4}{s+t}\left(\partial_s\psi + \partial_t\psi\right) + \frac{2}{u}\,\partial_u\psi + \left(\partial_{ss}\psi + \partial_{tt}\psi + \partial_{uu}\psi\right) + 2\,\partial_{st}\psi + 2\,\frac{s\,t + u^2}{u\,(s+t)}\left(\partial_{su}\psi + \partial_{tu}\psi\right). \tag{4.3}$$

The operator with respect to y can be obtained by changing t→-t:

$$\Delta_y\,\psi = \frac{4}{s-t}\left(\partial_s\psi - \partial_t\psi\right) + \frac{2}{u}\,\partial_u\psi + \left(\partial_{ss}\psi + \partial_{tt}\psi + \partial_{uu}\psi\right) - 2\,\partial_{st}\psi + 2\,\frac{-s\,t + u^2}{u\,(s-t)}\left(\partial_{su}\psi - \partial_{tu}\psi\right). \tag{4.4}$$

The kinetic part of the Schrödinger equation takes the form

$$\begin{aligned}\frac{1}{2}\left(\triangle_x\psi+\triangle_y\psi\right) &= (\partial_{ss}\psi+\partial_{tt}\psi+\partial_{uu}\psi)+\frac{2}{u}\partial_u\psi+\frac{4}{s^2-t^2}(s\,\partial_s\psi-t\,\partial_t\psi)+\\&+\frac{2s}{s^2-t^2}\,\frac{1}{u}\left(u^2-t^2\right)\partial_{su}\psi+\frac{2t}{s^2-t^2}\,\frac{1}{u}\left(s^2-u^2\right)\partial_{tu}\psi\,.\end{aligned}\tag{4.5}$$

The Schrödinger equation takes the form (in atomic units)

$$\begin{aligned}E\,\psi &= -(\partial_{ss}\psi+\partial_{tt}\psi+\partial_{uu}\psi)-\frac{2}{u}\partial_u\psi-\frac{4}{s^2-t^2}(s\,\partial_s\psi-t\,\partial_t\psi)\\&-\frac{2s}{s^2-t^2}\,\frac{1}{u}\left(u^2-t^2\right)\partial_{su}\psi+\frac{2t}{s^2-t^2}\,\frac{1}{u}\left(s^2-u^2\right)\partial_{tu}\psi-\frac{4Zs}{s^2-t^2}\psi+\frac{1}{u}\psi\end{aligned}$$

or

$$\begin{aligned}&u\left(s^2-t^2\right)(\partial_{ss}\psi+\partial_{tt}\psi+\partial_{uu}\psi)+2\left(s^2-t^2\right)\partial_u\psi+\\&4u\,(s\,\partial_s\psi-t\,\partial_t\psi)+2s\left(u^2-t^2\right)\partial_{su}\psi+2t\left(s^2-u^2\right)\partial_{tu}\psi+\\&4Zus\psi-\left(s^2-t^2\right)\psi=-Eu\left(s^2-t^2\right)\psi.\end{aligned}\tag{4.6}$$

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# Problem 5

*Write in terms of Hylleraas variables the mean energy of the Hamiltonian on a spherical symmetric state. Write the Schrödinger equation resulting from the variational principle and compare with the result of previous problem.*

## Solution

We use the notation of the text and of the previous problem. The Hylleraas variables are defined by

$$s=r_1+r_2\,;\;t=r_1-r_2\,;\;u=r_{12};\qquad 0\le t\le u\le s\le\infty\tag{5.1}$$

If (r, $\theta$, $\varphi$) the angular coordinates for each electron and $\gamma$ is the angle between the directions between the two vectors $\mathbf{x}_1$and $\mathbf{x}_2$:

$$r_{12}^2=r_1^2+r_2^2-2\,r_1\,r_2\,\mathrm{Cos}[\gamma];\qquad \mathrm{Cos}[\gamma]=\mathrm{Cos}[\theta_1]\,\mathrm{Cos}[\theta_2]+\mathrm{Sin}[\theta_1]\,\mathrm{Sin}[\theta_2]\,\mathrm{Cos}[\varphi_2-\varphi_1]\,.$$

From (1) and this relation one get easily the relations

$$\begin{aligned}&r_1^2+r_2^2=\frac{s^2+t^2}{2};\qquad 2\,r_1\,r_2=\frac{s^2-t^2}{2};\\&\frac{1}{r_1}+\frac{1}{r_2}=\frac{r_1+r_2}{r_1\,r_2}=\frac{4s}{s^2-t^2};\qquad \frac{1}{r_1}-\frac{1}{r_2}=\frac{r_2-r_1}{r_1\,r_2}=-\frac{4t}{s^2-t^2};\\&1-\mathrm{Cos}[\gamma]=2\,\frac{u^2-t^2}{s^2-t^2};\;1+\mathrm{Cos}[\gamma]=2\,\frac{s^2-u^2}{s^2-t^2}\;.\end{aligned}\tag{5.2}$$

We want to write in term of s, t, u variables

$$\frac{\langle\psi\mid H\mid\psi\rangle}{\langle\psi\mid\psi\rangle}=E.\tag{5.3}$$

### The jacobian

First we compute the jacobian from cartesian to Hylleraas variables. Integrating on inessential angles:

$$d^3x_1\,d^3x_2=(4\pi)\,(2\pi)\,r_1^2\,r_2^2\,dr_1\,dr_2\,d\,(\mathrm{Cos}[\gamma])\,.$$

From previous relations

$$r_1^2\,r_2^2=\frac{\left(s^2-t^2\right)^2}{4};\;\mathrm{Cos}[\gamma]=\frac{s^2+t^2-u^2}{s^2-t^2}.$$

A simple computation gives

$$\frac{\partial(r_1,\ r_2,\ \text{Cos}[\gamma])}{\partial(s,\ t,\ u)} = \det\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ * & * & -\frac{u}{s^2-t^2} \end{pmatrix} = \frac{1}{2}\,\frac{u}{s^2-t^2}.$$

Then the volume element can be written (for spherical symmetric states) :

$$d^3 x_1\, d^3 x_2 = 8\,\pi^2\, \frac{\left(s^2-t^2\right)^2}{4}\, \frac{1}{2}\, \frac{u}{s^2-t^2}\, ds\, dt\, du = \pi^2\, u\, \left(s^2-t^2\right)\, ds\, dt\, du. \tag{5.4}$$

As only even - even and odd - odd (in t) matrix elements can be computed (i.e. between symmetric and antisymmetric wave functions) we can limit the t integration to the region $t > 0$ and use the expression (4) with an additional factor 2 in front.

### ■ The quadratic forms

The Hamiltonian, and the mass correction term (see text and problem 3) can be written in terms of the following quadratic forms

$$\mathbf{M} = \frac{1}{2}\int\left(\left(\nabla_1\Psi\right)^2 + \left(\nabla_2\Psi\right)^2\right);\quad \mathbf{L} = \int\left(\frac{Z}{r1} + \frac{Z}{r2} - \frac{1}{r12}\right)\Psi^2;\quad \mathbf{N} = \int\Psi^2;\quad \mathbf{K} = \int\left(\left(\nabla_1\Psi\right)\left(\nabla_2\Psi\right)\right); \tag{5.5}$$

The forms L and N are elementary. A part an overall coefficient $\left(2\,\pi^2\right)$

$$\boldsymbol{L} = \int_0^\infty ds \int_0^s du \int_0^u dt\left(4\,Z\,u\,s - \left(s^2-t^2\right)\right)\Psi^2;$$

$$\boldsymbol{N} = \int_0^\infty ds \int_0^s du \int_0^u dt\, u\left(s^2-t^2\right)\Psi^2;$$

The computation of M and K is a bit more laborious. Using the result of previous problem and indicating with x, y the coordinates of first and second electron:

$$\frac{\partial}{\partial x^i}\psi = \frac{x^i}{r_1}\partial_s\psi + \frac{x^i}{r_1}\partial_t\psi + \frac{x^i-y^i}{r_{12}}\partial_u\psi;$$

$$\frac{\partial}{\partial y^i}\psi = \frac{y^i}{r_2}\partial_s\psi - \frac{y^i}{r_2}\partial_t\psi - \frac{x^i-y^i}{r_{12}}\partial_u\psi;$$

A bit of work, or a look at notebook NB-10.15, allow to write using these relations:

$$\begin{aligned}\boldsymbol{M} = \int_0^\infty ds \int_0^s du \int_0^u dt\Bigg(\ & s\left(u^2-t^2\right)\left(\frac{\partial\Psi}{\partial s}\frac{\partial\Psi}{\partial u} + \frac{\partial\Psi}{\partial s}\frac{\partial\Psi}{\partial u}\right) + \\ & t\left(s^2-u^2\right)\left(\frac{\partial\Psi}{\partial t}\frac{\partial\Psi}{\partial u} + \frac{\partial\Psi}{\partial t}\frac{\partial\Psi}{\partial u}\right) + \left(s^2-t^2\right)u\left(\frac{\partial\Psi}{\partial s}\frac{\partial\Psi}{\partial s} + \frac{\partial\Psi}{\partial t}\frac{\partial\Psi}{\partial t} + \frac{\partial\Psi}{\partial u}\frac{\partial\Psi}{\partial u}\right)\Bigg);\end{aligned}$$

$$\boldsymbol{K} = \int_0^\infty ds \int_0^s du \int_0^u dt\left(-2\,s\left(u^2-t^2\right)\left(\frac{\partial\Psi}{\partial u}\frac{\partial\Psi}{\partial s}\right) + u\left(s^2+t^2-2\,u^2\right)\left(\left(\frac{\partial\Psi}{\partial s}\right)^2 - \left(\frac{\partial\Psi}{\partial t}\right)^2\right) - 2\,t\left(s^2-u^2\right)\left(\frac{\partial\Psi}{\partial u}\frac{\partial\Psi}{\partial t}\right) - u\left(s^2-t^2\right)\left(\frac{\partial\Psi}{\partial u}\right)^2\right);$$

### ■ Variational principle

Variational principle implies

$$\frac{\delta M}{\delta\psi} - \frac{\delta L}{\delta\psi} - E\,\frac{\delta N}{\delta\psi} = 0 \tag{5.6}$$

In performing the variations one has to remember that M is a symmetric form. A short calculation gives

$$\frac{1}{2}\frac{\delta L}{\delta\psi} = \left(4\,Z\,u\,s - \left(s^2-t^2\right)\right)\psi;\quad \frac{1}{2}\frac{\delta N}{\delta\psi} = u\left(s^2-t^2\right)\psi;$$

$$\begin{aligned}\frac{1}{2}\frac{\delta M}{\delta\psi} = \\ & u\left(s^2-t^2\right)\left(\partial_{ss}\psi + \partial_{tt}\psi + \partial_{uu}\psi\right) + 2\left(s\left(u^2-t^2\right)\partial_{su}\psi + t\left(s^2-u^2\right)\partial_{tu}\psi\right) + 2\,u\,s\,\partial_s\psi - 2\,u\,t\,\partial_t\psi + \left(s^2-t^2\right)\partial_u\psi + \\ & \quad \left(2\,u\,s\,\partial_s\psi - 2\,t\,u\,\partial_t\psi\right) + \left(u^2-t^2\right)\partial_u\psi + \left(s^2-u^2\right)\partial_u\psi = \\ & u\left(s^2-t^2\right)\left(\partial_{ss}\psi + \partial_{tt}\psi + \partial_{uu}\psi\right) + 2\left(s\left(u^2-t^2\right)\partial_{su}\psi + t\left(s^2-u^2\right)\partial_{tu}\psi\right) + 4\,u\,s\,\partial_s\psi - 4\,t\,u\,\partial_t\psi + 2\left(s^2-t^2\right)\partial_u\psi.\end{aligned}$$

Substitution in (6) gives

$$u\left(s^2-t^2\right)\left(\partial_{ss}\psi + \partial_{tt}\psi + \partial_{uu}\psi\right) + 2\left(s^2-t^2\right)\partial_u\psi +$$

$$4\,u\,(s\,\partial_s\psi - t\,\partial_t\psi) + 2\,s\,(u^2 - t^2)\,\partial_{su}\psi + 2\,t\,(s^2 - u^2)\,\partial_{tu}\psi + 4\,Z\,u\,s\psi - (s^2 - t^2)\,\psi = -E\,u\,(s^2 - t^2)\,\psi.$$

The same result obtained in previous problem.

## Problem 6

*Write the effective Hamiltonian for the relativistic corrections in S states of helium. Compute the effect on the ground state using the simplest variational wave function. (For the general atomic Hamiltonian see Complements of chapter 14).*

### Solution

The general form of the Hamiltonian for an atom is

$$H = H_0 + H_1 + U_{LS} + U_{ee}^{(1)} + U_{ee}^{(2)} + \mathcal{O}\left(\frac{m^2}{M^2}, \frac{m}{M}\alpha^2\right). \tag{6.1}$$

m and M are electron and nucleus mass. $\alpha$ is the fine structure constant. The various operators are:

$$H_0 = \sum_a \frac{p_a^2}{2\,\mu} - \sum_a \frac{Ze^2}{r_a}; \tag{6.2}$$

$$H_1 = -\sum_a \left(\frac{p_a^4}{8\,c^2\,\mu^3} + \pi\frac{Z\,e^2\,\hbar^2}{2\,m^2\,c^2}\,\delta^{(3)}[\mathbf{r}_a]\right); \tag{6.3}$$

$$U_{LS} = \sum_a \frac{Z\,e^2\,\hbar^2}{4\,m^2\,c^2}\,\frac{1}{r_a^3}\,\mathbf{L}_a\cdot\mathbf{s}_a\,; \tag{6.4}$$

$$U_{ee}^{(1)} = -\sum_{a<b} \frac{e^2}{2\,m^2\,c^2\,r_{ab}}\left(\mathbf{p}_a\cdot\mathbf{p}_b + \mathbf{n}_{ab}\,(\mathbf{n}_{ab}\cdot\mathbf{p}_a)\,\mathbf{p}_b\right) - \sum_{a<b}\pi\frac{e^2\,\hbar^2}{m^2\,c^2}\,\delta^{(3)}[\mathbf{r}_{ab}] + \frac{1}{M}\sum_{a<b}\mathbf{p}_a\cdot\mathbf{p}_b; \tag{6.5}$$

$$U_{ee}^{(2)} = \sum_{a<b}\frac{e^2\,\hbar}{4\,m^2\,c^2\,r_{ab}^2}\left(-(\boldsymbol{\sigma}_a + 2\,\boldsymbol{\sigma}_b)\cdot(\mathbf{n}_{ab}\wedge\mathbf{p}_a) + (\boldsymbol{\sigma}_b + 2\,\boldsymbol{\sigma}_a)\cdot(\mathbf{n}_{ab}\wedge\mathbf{p}_b)\right. + \tag{6.6}$$

$$+\sum_{a<b}\frac{e^2\,\hbar}{4\,m^2\,c^2}\left(\frac{\boldsymbol{\sigma}_a\cdot\boldsymbol{\sigma}_b - 3\,(\boldsymbol{\sigma}_a\cdot\mathbf{n}_{ab})\,(\boldsymbol{\sigma}_b\cdot\mathbf{n}_{ab})}{r_{ab}^3} - \boldsymbol{\sigma}_a\cdot\boldsymbol{\sigma}_b\,\frac{8\,\pi}{3}\,\delta^{(3)}[\mathbf{r}_{ab}]\right) \tag{6.7}$$

$\mathbf{n}_{ab}$ is the unit vector from particle b to particle a. $\sigma$ are Pauli matrices. The sums run on electrons.

We want to extract from this general form the effective Hamiltonian for S states in helium.

1. The first two terms in $U_{ee}^{(2)}$ have no first order contribution in S states as they transform respectively as a vector and a traceless symmetric tensor (L=2). The Wigner-Eckart theorem implies that their mean value on S states is zero.
2. A similar result holds for $U_{LS}$ as **L**|L=0⟩ = 0.
3. Finally we note that

$$\frac{1}{4}\,\boldsymbol{\sigma}_a\cdot\boldsymbol{\sigma}_b = \frac{S\,(S+1)}{2} - \frac{3}{4} = \begin{cases} -\frac{3}{4} & \text{singlet} \\ \frac{1}{4} & \text{triplet} \end{cases}$$

The final form of the relativistic corrections can then be written as (we use atomic units):

$$V = V_1 + V_2 + V_3 + V_4 + V_5 \tag{6.8}$$

$$
\begin{aligned}
&V_1 = -\frac{\alpha^2}{8}\left(p_1^4 + p_2^4\right);\\
&V_2 = -\frac{\alpha^2}{2}\,\frac{1}{r_{12}}\left(\mathbf{p}_1\cdot\mathbf{p}_2 + \mathbf{n}_{12}\left(\mathbf{n}_{12}\cdot\mathbf{p}_1\right)\mathbf{p}_2\right);\\
&V_3 = Z\,\frac{\pi\,\alpha^2}{2}\left(\delta[\mathbf{r}_1] + \delta[\mathbf{r}_2]\right);\\
&V_4 = c_S\,\pi\,\alpha^2\,\delta[\mathbf{r}_{12}];\;\; c_S = (1, -5/3) \text{ for } (\text{singlet, triplet});\\
&V_5 = \frac{1}{M}\,\mathbf{p}_1\cdot\mathbf{p}_2;
\end{aligned}
\tag{6.9}
$$

- **Ground state correction**

We use

$$
\psi\,(x_1, x_2) = \varphi\,(r_1)\,\varphi\,(r_2);\quad \varphi[r] = \frac{1}{\sqrt{\pi}}\,Z_1^{3/2}\,\mathrm{Exp}[-Z_1\,r];\quad Z_1 = Z - \frac{5}{16}. \tag{6.10}
$$

These functions are the same as the ground state hydrogen functions with effective charge $Z_1$. Using the identity valid for hydrogenic functions

$$
\frac{p^2}{2}\,|n\rangle = \left(-\frac{Z_1^2}{2\,n^2} + \frac{Z_1}{r}\right)|n\rangle,
$$

all matrix elements on the ground state are easily calculable, we have

$$
\langle V_1\rangle = -\frac{5}{4}\,\alpha^2\,Z_1^4;\;\; \langle V_3\rangle = \alpha^2\,Z_1^3\,Z;\;\; \langle V_4\rangle = \frac{1}{8}\,\alpha^2\,Z_1^3;\;\; \langle V_2\rangle = \langle V_5\rangle = 0.
$$

It is interesting to compute the correction to ionization potential. The helium ion is an hydrogen-like atom with charge Z, the result is the same as before with $Z_1$substituted with Z and a factor 1/2 in front all terms (we have only one electron in the ion), it follows

$$
\delta E_{\text{ion}} = -\frac{1}{8}\,Z^4\,\alpha^2. \tag{6.11}
$$

The result for Z = 1 agree with the known result for hydrogen (see chapter on perturbation theory).

The relativistic correction to ionization potential is

$$
\delta J = \delta E_{\text{ion}} - \delta E. \tag{6.12}
$$

In the table below we list the various contributions for helium (Z = 2) in units of $\alpha^2$

| | ion | $V_1$ | $V_2$ | $V_3$ | $V_4$ | $V_5$ | tot |
|---|---|---|---|---|---|---|---|
| $\delta E$ | | -10.1 | 0 | 9.6 | 0.6 | 0 | 0.075 |
| $\delta J$ | -2 | 10.1 | 0 | -9.6 | -0.6 | 0 | -2.07 |

We see a strong cancellations which lower the total result. A more accurate computation is given in the notebooks. This cancellation is one of the reason why the Lamb shift correction for helium is relatively important.

# Problem 7

*Consider a generic interval [a,b] and a measure μ[x]dx on this interval. Assume that all moments exist, i.e.* $x^n$*are integrables. On the Hilbert space* $\mathbb{L}^2$*[μ;a,b] one can define a complete base of polynomials (Weierstrass' theorem).*

1. Show that the basis can be made orthogonal and that multiplication by the variable x on a polynomial of degree n can be expressed as a linear combination of polynomials of degrees n+1, n , n-1.
2. Interpret this relation as a Hilbert space realization (matrix realization) of x operator and show that considering a finite dimensional approximation of this representation one can prove Gauss' summation formulas, i.e. the approximations of integrals by means of abscissas and weights of the relative polynomial class.

## ● Solution

- **Construction of the basis**

The first question is easily answered by the Gram-Schmidt orthogonalization procedure. We assume that μ has been normalized with (integration's limit are always assumed a and b, the extremal points of the interval)

$$\int \mu[x]\, dx = 1$$

and we will use the notation

$$\langle f \mid g \rangle = \int dx\, \mu[x]\, f[x]\, g[x]\,.$$

The polynomial

$$f_0[x] = 1 \qquad (7.1)$$

is taken as the first element of the basis. Subsequent elements are constructed by induction, multiplying by x and subtracting the projection on subspaces already constructed:

$$f_1[x] = C_1\,(x\, f_0[x] - \langle x\, f_0[x] \mid f_0 \rangle\, f_0[x])$$

$$f_n[x] = C_n \left( x\, f_{n-1}[x] - \sum_{k=0}^{n-2} \langle x\, f_{n-1} \mid f_k \rangle\, f_k[x] \right). \qquad (7.2)$$

$C_n$ is a normalization factor.

The recurrence relation follows from induction. It is trivially true for n=1, x $f_1$is a second order polynomial and can be written as

$$x\, f_1 = a\, f_2 + b\, f_1 + c\, f_0$$

for higher order follows from induction and use of (2) once observed that

$$\langle x\, f_{n-1} \mid f_k \rangle = \langle f_{n-1} \mid x\, f_k \rangle$$

The operator x, inthe sense of matrix element between basis vectors, is hermitian, than the recurrence relation has the form

$$x\, f_n = a_{n+1}\, f_{n+1} + b_n\, f_n + a_{n-1}\, f_{n-1} \qquad (7.3)$$

In matrix form

$$\begin{array}{c|ccccccc}
 & f_0 & f_1 & . & . & . & f_n & \\
\hline
f_0 & b_0 & a_1 & 0 & . & . & . & . \\
f_1 & a_1 & b_1 & a_2 & . & . & . & . \\
. & 0 & . & . & . & . & . & . \\
. & . & . & . & . & . & . & . \\
. & . & . & . & . & . & a_n & 0 \\
f_n & . & . & . & . & a_n & b_n & . \\
 & . & . & . & . & 0 & . & .
\end{array}$$

### The Gauss formulas

Suppose we diagonalize x matrix, let $\mid x_i \rangle$ the eigenvectors. On these eigenvectors f[x] $\mid x_i \rangle = f[x_i] \mid x_i \rangle$. Formally we have

$$\int \mu[x]\, F[x]\, dx = \int \mu[x]\, f_0\, F[x]\, f_0\, dx = \langle f_0 \mid x_i \rangle \left\langle x_i \middle| F[x] \middle| x_j \right\rangle \left\langle x_j \middle| f_0 \right\rangle = \sum_{x_i} F[x_i]\, \delta_{ij}\, \langle f_0 \mid x_i \rangle \left\langle x_j \middle| f_0 \right\rangle = \sum_{x_i} F[x_i]\, \langle f_0 \mid x_i \rangle^2 \equiv \sum w_i\, F[x_i]\,. \qquad (7.4)$$

The weights $w_i$are the square of the first component of the eigenvectors $\mid x_i \rangle$. This formula, as it stands, does not make much sense as x has a continuous spectrum but, once truncated, eq.(4) are just Gauss formulas, which can be resumed as follows:

Given a measure $\mu$[x] and an orthogonal set of polynomials $f_k$ with respect this measure, than Gauss integration formula with n points is

$$\int \mu[x]\, F[x]\, dx = \sum_{i=0}^{n-1} w_i\, F[x_i] \qquad (7.5)$$

1. The n points $x_i$ are the roots of the polynomial of degree n (it can be shown that they lie all in the interval).
2. These points are the eigenvalues of the matrix n×n written above.
3. The weights are the square of the first component of the eigenvectors of that matrix, let us call M that n×n matrix.

The Gauss formulas are closely related to properties of tridiagonal matrices and these, in turn are those properties which have repeatedly used in several problems from the beginning of our study, in essence the operator x *connect only neighboring states*. We have to prove that in fact the truncation of Hilbert space give rise to all listed properties.

We assume that matrix X has n distincts eigenvalues, also this can be proven. Let $\varphi_k$ its eigenvectors and $x_k$its eigenvalues. In Schrödinger representation the eigenvectors are polynomial, being linear combination of basis functions, which were polynomials.

**N.B.** The index we are using for polynomials is its degree, than starts from zero. The matrix n×n taken above is constructed on the first n states, i.e. on polynomials of degree 0,1, ... n-1, i.e. up to degree n-1

$$\varphi_k[x] = \sum_{s=0}^{n-1} C_s^{(k)}\, f_s[x] \qquad (7.6)$$

The matrix C is orthogonal, as we are working with real functions. On the eigenstates $f_s$we have, as a matrix

$$M\,\varphi_k[x] = x_k\,\varphi_k[x]; \quad \text{i.e.} \quad \sum_{j=0}^{n-1} M_{sj}\, C_j^{(k)} = x_k\, C_s^{(k)} \qquad (7.7)$$

The equation (7) **is not** an exact relation at operators level, but is only an approximate realization of operator x, in our subspace of dimension n. But the correction is quite mild and of a special form. In fact, as multiplication by x at most raises by one the index of the basis vectors, the relation is wrong at most by a missing factor $f_n$, the next to last element of those considere din our base. Than *as exact* expression we have

$$x\,\varphi_k[x] = x_k\,\varphi_k[x] + \alpha^{(1)}\, f_n[x]. \qquad (7.8)$$

We stress again that this equation has a correction factor which is **only** $f_n$nor other polynomials. If we multiply eq(8) by x, a new $f_n$can appear, while the term already present can give rise only to terms $f_n$, $f_{n-1}$, $f_{n+1}$ for the recurrence relation on x. If we write $\mathcal{R}_a$ for a linear combination of basis polynomials with indexes ≥ a we have the following structure

$$x^s\,\varphi_k[x] = x_k^s\,\varphi_k[x] + \mathcal{R}_{n-s+1} \qquad (7.9)$$

Consider now the function 1, i.e. the first basis polynomial. This is part of our subspace than the exact relation exists

$$1 = \sum_{k=0}^{n-1} d_k\,\varphi_k[x]; \quad d_k = C_0^{(k)}. \qquad (7.10)$$

The value of the coefficient comes from the orthonormality of the basis and from eq.(6). Multiplying equation (6) by $x^s$and using (9) and linearity we have for a generic polynomial G of degree M

$$G[x] = \sum_m a_m\, x^m = \sum_{k=0}^{n-1} d_k \sum_m a_m\, x_k^m\,\varphi_k[x] + \sum \mathcal{R}_{n-m+1} = \sum_{s=0}^{n-1} d_k\, G[x_k]\,\varphi_k[x] + \mathcal{R}_{n-M+1} \qquad (7.11)$$

In exactly the same way from (9) it follows

$$G[x]\,\varphi_k[x] = G[x_k]\,\varphi_k[x] + \mathcal{R}_{n-M+1} \qquad (7.12)$$

We have now the first important property. Take for G the polynomial $f_n$[x]. The remainder in (12) is $\mathcal{R}_1$ i.e. it is a combination of basis functions of index greater or equal to one, its integral vanishes. The same is true for the left hand side of the equation as $f_n$ is orthogonal to the subspace of polynomial of degree less than n, it follows, integrating

$$0 = G[x_k]\,\langle f_0 \mid \varphi_k\rangle \Rightarrow G[x_k] = 0 \qquad (7.13)$$

The coefficients are all nonzero: as it is to show every tridiagonal matrix with $a_i$(see table) non zero cannot have eigenvectors with vanishing first component, then our implication is correct. This means that $f_n$vanishes on the n points $x_k$ (assumed distinct) than these points are its roots: *the eigenvalues of the n×n matrix M are the root of the n-th polynomial*. This is the first of the properties to be proven.

Now let come back to eq. (11). Assume that G is any basis vector $f_s$ except $f_0$ up to $f_n$, i.e. 1 ≤ s ≤ n. Integrating we have (as usual the remainder integrated vanishes):

$$0 = \sum_{k=0}^{n-1} d_k\, f_s[x_k] \int \mu[x]\,\varphi_k[x] = \sum_{k=0}^{n-1} d_k^{\,2}\, f_s[x_k] \qquad (7.14)$$

If we take $f_0$= 1 instead we have, for a normalized measure:

$$1 = \sum_{k=0}^{n-1} d_k^2 = 1 \tag{7.15}$$

because the $d_k$are the first row of an orthgonal matrix. Previous relations can proof the integration properties of Gauss formulas up to polynomials of order n, in fact any such polynomial can be written as

$$G = c_0 f_0 + \sum_{s=1}^{n} c_s f_s; \quad \int \mu[x] G[x] = c_0$$

This is just what follows from Gauss formula, with $d_k^2 = w_k$and relations (14) and (15):

$$\sum_{k=0}^{n-1} w_k G[x_k] = \sum_{k=0}^{n-1} w_k c_0 + \sum_{s=1}^{n} c_s \sum_{k=0}^{n-1} d_k{}^2 f_s[x_k] = c_0 .$$

Consider now polynomials up to degree 2 n - 1. A basis for these polynomials canbe taken by $f_s$with s≤n-1 and $g_s = f_n f_s$, i.e. we can write

$$G = \sum_{s=1}^{n-1} a_s f_s[x] + \sum_{s=1}^{n-1} b_s g_s[x]$$

In particular $f_j$ with j ≥ n canbe written in this way. The integral of $g_s$vanishes, being a product of $f_n$by a polynomial of less degree, then:

$$\int G[x] \mu[x] \, dx = a_0$$

Let us consider now Gauss formula. The first sum give $a_0$as result, as we have already seen,adding the second term:

$$\sum_{k=0}^{n-1} w_k G[x_k] = a_0 + \sum_{k=0}^{n-1} w_k \sum_{s=1}^{n-1} b_s f_n[x_k] f_s[x_k]$$

But $x_k$are roots of $f_n$the added term vanishes and Gauss formula is verified up to polynomials of degree 2n-1.

In conclusion Gauss formulas are just what we expect from a truncation of (4) with some bonus: we have shown that it is exact for a class of polynomial functions.