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Quantum Mechanics Based on Probability Wave Functions Induced by the Minimum Mean Deviation from Statistical Equilibrium. II

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The maximum-entropy probability distributions are generally used as probabilistic models for describing statistical equilibrium subject to given mean values of some random variables. This paper uses probability wave functions obtained by minimizing the mean deviation from statistical equilibrium subject to generalized moments and correlations, whose values are determined looking for stationary points of the mean energy of the quantum system. The results are applied to the study of the ground state of the helium and lithium atoms.

1. INTRODUCTION

The Schrödinger equation (Schrödinger, 1926) is included today among the postulates of nonrelativistic quantum mechanics. Its solution is the so-called wave function ψ of the corresponding quantum system. It was Born (1926) who interpreted $\psi^*\psi$ as being a probability density that may be used for making predictions about the behavior of quantum systems.

As the ultimate use of the Schrödinger equation is to provide us with probabilistic models for the behavior of quantum systems, a natural question comes up: Is it possible to build such probabilistic models without having to write and solve the corresponding Schrödinger equation? The question is even more justified if we take into account that the Schrödinger equation may be solved exactly only for a very limited number of quantum systems, namely the free particle in a box, the harmonic oscillator, and the hydrogen atom. The first part of this paper discussed the direct construction of a probabilistic model for quantum systems looking for the stationary values of

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the mean energy corresponding to the wave function obtained by minimizing the mean deviation from statistical equilibrium subject to given generalized correlations. The formalism was applied there to obtain the exact solutions for some quantum systems (one or two free particles in a box, the harmonic oscillator, the hydrogen atom) without using the corresponding Schrödinger equations. In this second part, the formalism is applied to obtain accurate approximations for the ground state of the helium and lithium atoms.

Summarizing, we start from statistical equilibrium described by a maximum-entropy probability distribution subject to constraints induced by given mean values of some random variables. This variational problem, known as the maximum entropy principle (MEP), is very well studied in the literature. Thus, on the positive real axis $[0, +\infty)$, the solution of MEP subject to the mean value μ is the exponential distribution $\mathbf{E}(\mu)$. On an arbitrary interval $[a, b]$ of the real axis, if we have no constraints attached, then the probability distribution of maximum entropy is the uniform distributions $\mathbf{U}(a,b)$. Once the probability distribution that describes statistical equilibrium is obtained, and u is its density, we choose a sequence of orthogonal functions with the weight u as a system of generalized coordinates. Such systems of orthogonal functions are the Laguerre polynomials for the exponential distribution $\mathbf{E}(\mu)$, the generalized Laguerre polynomials for the gamma distribution $\mathbf{G}(1/\alpha, \beta + 1)$, and either the trigonometric system or the Legendre (spherical) polynomials for the uniform distribution $\mathbf{U}(a,b)$. As long as the statistical equilibrium is not perturbed, the mean values of the generalized coordinates remain equal to zero. If, however, random perturbations induced by internal or/and external interactions alter the statistical equilibrium, then some of these mean values cease to be equal to zero. We minimize the mean deviation from statistical equilibrium subject to given generalized mean values. The mean deviation is measured using Pearson's χ^2 indicator from statistical inference. In general, a wave is just any disturbance to a field. In our context, we introduce a probability wave function to be the minimum deviation from statistical equilibrium due to random internal or/and external fluctuations. Once the probability wave function χ is obtained, the normed square of its absolute value is used as a probability density function on the set of possible configurations. In the multidimensional case, for incompatible entities (like position and momentum, for instance) it is senseless to talk about a joint probability distribution. For independent compatible entities (like the three components of the position of a particle in a three-dimensional Euclidean space, for instance), the joint probability density is simply the product of the probability densities (i.e., the marginals) of the corresponding entities. For dependent compatible entities (like the positions of several interacting particles, for instance), the joint probability distribution is not uniquely determined by the marginals and by the partial information available about their dependence (like some generalized mixed moments called generalized correlations, for instance). We construct the multidimensional probability wave obtained by minimizing the mean $\overline{\chi}^2$ deviation from the direct, independent product of the marginals subject to the given generalized correlations. Once the one-dimensional or multidimensional probability wave function is obtained by solving the above-mentioned variational problem, we determine the unknown generalized correlations (i.e., taken as variational parameters) looking for the stationary points of the mean energy of the quantum system. The formalism is applied to the study of the ground state of the helium and lithium atoms, and the approximations obtained are surprisingly good even when the number of variational parameters is small. The computation is not complicated and may be implemented using a normal personal computer.

To put what has just been said in a more technical form, let us recall that if u is a probability density function on the set $D \subseteq \mathbf{R}^1$, and $\{U_n,\ n = 0,1,\ldots\}$, $U_0 \equiv 1$, a sequence of orthonormal functions with the weight u, i.e.,

$$\langle U_n U_l u \rangle = \begin{cases} 1 & \text{if} \quad l = n \\ 0 & \text{if} \quad l \neq n \end{cases}$$

which implies that $\|U_n\| = 1$ for all n ($n = 0, 1, \ldots$), with $\langle U_0 u \rangle = 1$ and $\langle U_n u \rangle = 0$ for all n ($n = 1, 2, \ldots$). We call $\{U_n,\ n = 0, 1, \ldots\}$ a system of generalized coordinates associated to the probability density function u. The probability density of the uniform distribution $\mathbf{U}$ (a, b) is

$$u(x) = \frac{1}{b - a}, \qquad x \in [a, b]$$

A system of orthonormal polynomials with this weight is

$$U_n(x) = (2n + 1)^{1/2}\, P_n\left(\frac{2}{b - a}\, x - \frac{a + b}{b - a}\right) \qquad (n = 0, 1, \ldots)$$

where $P_n(x)$ is the Legendre (spherical) polynomial of degree n. The first ones are

$$P_0(x) = 1, \qquad P_1(x) = x,$$

$$P_2(x) = \frac{1}{2}(3x^2 - 1), \qquad P_3(x) = \frac{1}{2}(5x^3 - 3x),$$

$$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5(x) = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$

A system of orthonormal functions with the weight $u(x) = 1/a$ on $D = [0, a]$ is the trigonometric system

$$U_0 \equiv 1, \qquad U_n(x) = \sqrt{2}\sin\frac{n\pi}{a}x \qquad (n = 1,2, \ldots)$$

The probability density of the exponential distribution $\mathbf{E}(\mu)$ is

$$u(x) = \frac{1}{\mu}e^{-x/\mu}, \qquad x \varepsilon [0, +\infty)$$

A system of orthonormal polynomials with this weight is

$$U_n(x) = L_n\left(\frac{x}{\mu}\right) \qquad (n = 0,1, \ldots)$$

where $L_n(x)$ is the Laguerre polynomial of degree n. The first ones are

$$L_0(x) = 1, \qquad L_1(x) = -x + 1,$$

$$L_2(x) = \frac{1}{2}(x^2 - 4x + 2)$$

$$L_3(x) = \frac{1}{6}(-x^3 + 9x^2 - 18x + 6)$$

$$L_4(x) = \frac{1}{24}(x^4 - 16x^3 + 72x^2 - 96x + 24)$$

$$L_5(x) = \frac{1}{120}(-x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120)$$

The probability density of the gamma distribution $\mathbf{G}(1/\alpha, \beta + 1)$, with parameters α and $\beta + 1$, is

$$u(x) = \frac{1}{\alpha^{\beta+1}\Gamma(\beta + 1)}x^\beta e^{-x/\alpha}, \qquad x \varepsilon [0, +\infty),$$

where $\alpha = \mu/(\beta + 1)$. A system of orthonormal polynomials with this weight is

$$U_n(x) = \left(\frac{n!\,\Gamma(\beta + 1)}{\Gamma(\beta + n + 1)}\right)^{1/2} L_n^{(\beta)}\left(\frac{x}{\alpha}\right) \qquad (n = 0, 1, \ldots)$$

where $L_n^{(\beta)}(x)$ is the generalized Laguerre polynomial of degree n and order β. We have

$$L_n^{(k)}(x) = \sum_{l=0}^{n} (-1)^l \binom{n+k}{n-l} \frac{1}{l!} x^l, \qquad L_n(x) = L_n^{(0)}(x)$$

If u is a probability density function on the set $D \subseteq \mathbf{R}^1$ and $\{U_n, n = 0, 1, \ldots\}$, $U_0 \equiv 1$, a sequence of orthonormal functions with the weight u, i.e.,

$$\langle U_n U_l\, u\rangle = \begin{cases} 1 & \text{if} \quad l = n \\ 0 & \text{if} \quad l \neq n \end{cases}$$

which implies that $\|U_n\| = 1$ for all n ($n = 0, 1, \ldots$), with $\langle U_0 u\rangle = 1$, and $\langle U_n u\rangle = 0$ for all n ($n = 1, 2, \ldots$). We call $\{U_n, n = 0, 1, \ldots\}$ a system of generalized coordinates associated to the probability density function u. Details about the orthonormal polynomials mentioned above may be found in Abramowitz and Stegun (1972); they may be easily generated using the computer package MATHEMATICA (Wolfram, 1991).

Let u be a probability density on $D \subseteq \mathbf{R}^1$ and let $\{U_n, n = 0, 1, \ldots\}$, $U_0 \equiv 1$, be a sequence of orthonormal polynomials with the weight u. As mentioned before, as long as nothing alters the statistical equilibrium described by the probability density function u, we have $\langle U_n\, u\rangle = 0$ ($n = 1, 2, \ldots$), and also $\langle U_0\, u\rangle = \langle u\rangle = 1$. Very often, however, random fluctuations alter such a statistical equilibrium and the probability density function u has to be replaced by another probability density function. If the sequence $\{U_n, n = 0, 1, \ldots\}$ is complete with respect to the weight u, then another probability density function f on D may be written as

$$f = u\left(1 + \sum_{n=1}^{+\infty} c_n U_n\right)$$

where $c_n = \langle U_n\, f\rangle$ is the U_n-moment of f or the mean fluctuation in the direction U_n, and the sum is taken with respect to the values of n ($n = 1, 2, \ldots$). On the other hand, the solution of the quadratic program

$$\min_{f} \overline{\chi}^2 = \langle \chi^2 \rangle = \langle \left(\frac{f}{u} - 1\right)^2 u\rangle$$

subject to

$$\langle U_n f\rangle = c_n \qquad (n = 1, 2, \ldots, N)$$

is

$$f = u\left(1 + \sum_{n=1}^{N} c_n U_n\right)$$

In the multidimensional case, let u and v be two probability density functions on $D_1 \subseteq \mathbf{R}^1$ and $D_2 \subseteq \mathbf{R}^1$, respectively, and let $\{U_n, n = 0, 1, \ldots\}$ and $\{V_l, l = 0, 1, \ldots\}$ ($U_0 \equiv 1$, $V_0 \equiv 1$) be two complete systems of orthonormal functions on D_1 and D_2 with the weights u and v, respectively. If there is independence between marginals, then the joint probability density on $D_1 \times D_2$ is simply the direct product uv. But what happens if there is interdependence between the two components? Consider the system of functions $\{U_nV_l; n, l = 0, 1, \ldots\}$ on $D_1 \times D_2$ with the weight uv. A joint probability density function f on $D_1 \times D_2$ has the form

$$f = uv\left(1 + \sum_{\substack{n=0 \\ (n,l)\neq(0,0)}}^{+\infty} \sum_{l=0}^{+\infty} c_{nl} U_n V_l\right)$$

Such a joint probability density function is the closest one, in the $\overline{\chi^2}$ sense, to the direct independent product uv subject to the generalized mixed moments (or generalized correlations)

$$c_{nl} = \langle U_n V_l f \rangle$$

Indeed, let

$$\chi = \frac{f - uv}{\sqrt{uv}} = \left(\frac{f}{uv} - 1\right)\sqrt{uv}$$

be the weighted deviation of f from the independent direct product uv. The solution of the quadratic program

$$\min_f \overline{\chi^2} = \langle \chi^2 \rangle$$

subject to

$$\langle U_n V_l f \rangle = c_{nl}, \qquad (n = 0, 1, \ldots, N; \quad l = 0, 1, \ldots, L; \quad (n,l) \neq (0, 0))$$

is the density

$$f = uv\left(1 + \sum_{\substack{n=0 \\ (n,l)\neq(0,0)}}^{N} \sum_{l=0}^{L} c_{nl} U_n V_l\right)$$

The generalization to more than two components is straightforward.

2. THE GROUND STATE OF THE HELIUM ATOM

As it is not possible to solve the Schrödinger equation exactly for any atom or molecule more complicated than the hydrogen atom, approximate methods, such as perturbation theory and the variational method, are used instead. For the helium atom, for instance, the corresponding Schrödinger equation cannot be solved exactly.

The helium atom has a nucleus and two electrons. Fixing the nucleus at the origin of a three-dimensional Euclidean coordinate system (x, y, z), the Hamiltonian operator has the form

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{12}}$$

where

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

is the Laplacian operator for electron $i \, (i = 1, 2)$, r_i is the radial distance from the nucleus (the origin) to electron i, r_{12} is the distance between the two electrons, m is the electronic mass, and $\hbar$, e, ε_0 are constants. Using atomic units, i.e., taking $\hbar = 1$, $m = 1$, e $= 1$, $4\pi\varepsilon_0 = 1$, the Hamiltonian becomes

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \left(\frac{2}{r_1} + \frac{2}{r_2}\right) + \frac{1}{r_{12}} \tag{1}$$

For such a quantum system the variational method provides an upper bound to its ground-state energy. The ground-state wave function ψ_0 and energy E_0 satisfy $\hat{H}\psi_0 = E_0\psi_0$, where $\hat{H}$ is the Hamiltonian operator of the system. According to the variational principle, for any other function ψ we have $E_\psi \geq E_0$, with

$$E_\psi = \frac{\langle \psi^* \hat{H} \psi \rangle}{\langle \psi^* \psi \rangle}$$

where ψ^* is the complex conjugate of ψ. The trial function ψ is chosen such that it depends on some arbitrary parameters $\alpha, \beta, \gamma, \ldots$, in which case E_ψ also will depend on these variational parameters, $E_\psi(\alpha, \beta, \gamma, \ldots) \geq E_0$. The variational parameters are determined in order to minimize $E_\psi(\alpha, \beta, \gamma, \ldots)$. There is no unique or optimal way of selecting the trial function ψ in the literature. The first trial function of interest was introduced 69 years ago by Hylleraas (1929), namely,

$$\psi(r_1, r_2, r_{12}) = e^{-\alpha r_1} e^{-\alpha r_2}[1 + P(r_1, r_2, r_{12})] \tag{2}$$

where P is a polynomial in r_1, r_2, r_{12} whose coefficients, together with α, are taken as variational parameters. No theoretical justification of this choice was given, but it proved to give a value of the ground energy of the helium atom in very accurate agreement with the experimental value. Reminiscences of the early quantum mechanics of two-electron atoms may be found in the very well-written paper by Hylleraas (1963). Since 1929, many generalizations of Hylleraas' approach have been proposed, but again, without a sound theoretical justification. Trial functions of the form (2) proposed in the literature contained more and more variational parameters in the expression of the polynomial $P(r_1, r_2, r_{12})$ namely, 39 in Kinoshita (1957) and even 1078 in Pekeris (1959). Details may be found in McQuarrie (1983, p. 291).

The objective of this section is to show that the general formalism discussed in the first part of the paper may be applied for approximating the ground-state energy of the helium atom. The case of one electron was discussed in Section 7 of the first part. For the helium atom, we deal with a system of two interdependent electrons with random behavior. Switching from the Cartesian coordinates $(x_1, y_1, z_1, x_2, y_2, z_2)$ to the spherical coordinate system

$$x_i = r_i \sin\theta_i \cos\omega_i, \qquad y_i = r_i \sin\theta_i \sin\omega_i,$$
$$z_i = r_i \cos\omega_i, \qquad (i = 1, 2)$$
$$0 \le r_i < +\infty, \qquad 0 \le \theta_i \le \pi, \qquad 0 \le \omega_i \le 2\pi \qquad (i = 1, 2)$$

and eventually changing to variables $s_i = \cos\theta_i$ $(i = 1, 2)$, with $-1 \le s_i \le 1$, the joint probability density of the system formed by the two electrons of the helium atom is

$$\begin{aligned}
& g(x_1, y_1, z_1; x_2, y_2, z_2)\, dx_1\, dy_1\, dz_1\, dx_2\, dy_2\, dz_2 \\
&\quad = f(r_1, s_1, \omega_1; r_2, s_2, \omega_2)\, r_1^2\, r_2^2\, dr_1\, ds_1\, d\omega_1\, dr_2\, ds_2\, d\omega_2 \\
&\quad = f_1(r_1, s_1, \omega_1)\, f_2(r_2, s_2, \omega_2) \\
&\qquad \times \Big[1 + \sum_{(n,l,k,n',l',k') \ne (0,0,0,0,0,0)} c_{nlk,n'l'k'} U_n(r_1) V_l(s_1) W_k(\omega_1) \\
&\qquad \times U_{n'}(r_2) V_{l'}(s_2) W_{k'}(\omega_2)\Big] \\
&\qquad \times r_1^2 r_2^2\, dr_1\, ds_1\, d\omega_1\, dr_2\, ds_2\, d\omega_2
\end{aligned} \tag{3}$$

with

$$f_i(r_i, s_i, \omega_i) = M e(r_i) v(s_i) w(\omega_i) \qquad (i = 1, 2)$$

where $e(r) = (1/\mu)e^{-r/\mu}$ is the radial exponential probability density with parameter μ on $[0, +\infty)$;

$v(s) = 1/2$ is the uniform probability density on $[-1, 1]$;

$w(\omega) = 1/(2\pi)$ is the uniform probability density on $[0, 2\pi]$;

$f_i(r_i, s_i, \omega_i) = M(1/4\pi\mu)e^{-r_i/\mu}$, where M is a constant which may be found using the useful formula

$$\int_0^{+\infty} r^n e^{-r/\mu} dr = n!\mu^{n+1} \tag{4}$$

from the condition

$$1 = \langle f_i \rangle = \int_0^{+\infty} \int_{-1}^{+1} \int_0^{2\pi} f_i(r_i, s_i, \omega_i) r_i^2 dr_i ds_i d\omega_i = 2\, M\, \mu^2$$

implying $M = 1/(2\mu^2)$, which gives

$$f_i(r_i, s_i, \omega_i) = \frac{1}{8\pi\mu^3} e^{-r_i/\mu} \qquad (i = 1, 2) \tag{5}$$

Further

$$u(r) = \frac{1}{2\mu^2} r^2\, e(r) = \frac{1}{2\mu^3} r^2 e^{-r/\mu}$$

is the radial gamma distribution with parameters μ and 3 on $[0, +\infty)$;

$U_n(r)$ is the second-order Laguerre polynomial $L_n^{(2)}(r/\mu)$ of degree n, with $U_0 \equiv 1$;

$V_l(s)$ is the Legendre polynomial $(2l + 1)^{1/2} P_l(s)$ of degree l, with $V_0 \equiv 1$; and

$W_k(\omega)$ is the trigonometric function $\sqrt{2} \sin(k\,\omega/2)$, with $W_0 \equiv 1$.

The corresponding joint and marginal probability wave functions are

$$\psi = \sqrt{f}, \qquad \psi_i = \sqrt{f_i} \qquad (i = 1, 2)$$

respectively. Thus,

$$\psi_i(r_i, s_i, \omega_i) = \frac{1}{\sqrt{8\pi\mu^3}} e^{-r_i/(2\mu)}$$

depending only on r_i. Using the approximation $\sqrt{1 + t} \approx 1 + (1/2)t$, which gives good results for small values of t, an approximation of the joint probability wave function of the system of two electrons of the helium atom is

$$\begin{aligned} &\psi(r_1, s_1, \omega_1; r_2, s_2, \omega_2) \\ &\quad = \psi_1(r_1, s_1, \omega_1)\psi_2(r_2, s_2, \omega_2) \end{aligned}$$

$$\times \left[1 + \sum_{(n,l,k,n',l',k')\neq(0,0,0,0,0,0)} \frac{1}{2} c_{nlk,n'l'k'} U_n(r_1) V_l(s_1) W_k(\omega_1) \right.$$
$$\left. \times U_{n'}(r_2) V_{l'}(s_2) W_{k'}(\omega_2) \right] \tag{6}$$

which gives good results when the generalized correlation coefficients $c_{nlk,n'l'k'}$ have relatively small values. Let us take now some simple joint probability wave functions of type (6) into account and see how accurately they can describe the ground state of the helium atom.

2.1. The Ground Energy Using the First-Order Radial Generalized Correlation

We assume in this subsection that the two electrons are linearly dependent in terms of the radial variable r and denote $c = \frac{1}{2} c_{100,100}$, assuming that all the other generalized correlation coefficients $c_{nlk,n'l'k'}$ are equal to zero. The joint probability wave function (6) becomes

$$\psi(r_1, r_2) = \psi_1(r_1)\psi_2(r_2)[1 + cL_1^{(2)}(r_1/\mu)L_1^{(2)}(r_2/\mu)]$$
$$= \frac{1}{8\pi\mu^3} e^{-(r_1+r_2)/(2\mu)} \left[1 + c\left(3 - \frac{r_1}{\mu}\right)\left(3 - \frac{r_2}{\mu}\right)\right] \tag{7}$$

As ψ_1 depends only on the radial variable r_1, the corresponding Laplacian has the form

$$\nabla_1^2\psi_1 = \frac{d^2\psi_1}{dr_1^2} + \frac{2}{r_1}\frac{d\psi_1}{\mathrm{d}r_1} = \left(\frac{1}{4\mu^2} - \frac{1}{\mu r_1}\right)\psi_1$$

and from (7) we get

$$\nabla_1^2\psi = \frac{d^2\psi}{dr_1^2} + \frac{2}{r_1}\frac{d\psi}{dr_1}$$
$$= \left[\left(\frac{1}{4\mu^2} - \frac{1}{\mu r_1}\right) + c\left(\frac{33}{4\mu^2} - \frac{15}{\mu r_1} - \frac{3r_1 + 11r_2}{4\mu^3} + \frac{5r_2}{\mu^2 r_1}\right.\right.$$
$$\left.\left. + \frac{r_1 r_2}{4\mu^4}\right)\right]\psi_1(r_1)\psi_2(r_2)$$

Using (4) several times, we obtain

$$\langle\psi\nabla_1^2\psi\rangle = \int_0^{+\infty}\int_{-1}^{+1}\int_0^{2\pi}\int_0^{+\infty}\int_{-1}^{+1}\int_0^{2\pi} \psi\nabla_1^2\psi r_1^2 r_2^2 \, dr_1 \, ds_1 \, d\omega_1 \, dr_2 \, ds_2 \, d\omega_2$$

$$= -\frac{1}{4\mu^2}(1 + 21\, c^2) \tag{8}$$

Similarly, we get

$$\langle\psi \, \nabla_2^2 \, \psi\rangle = -\frac{1}{4\mu^2}(1 + 21\, c^2) \tag{9}$$

From (7), using again (4) several times, we obtain

$$\langle\psi \frac{1}{r_i} \psi\rangle = \int_0^{+\infty}\int_{-1}^{+1}\int_0^{2\pi}\int_0^{+\infty}\int_{-1}^{+1}\int_0^{2\pi} \frac{1}{r_i}\psi^2 r_1^2 r_2^2 \, dr_1 \, ds_1 \, d\omega_1 \, dr_2 \, ds_2 \, d\omega_2$$

$$= \frac{1}{2\mu}(1 + 9\, c^2) \qquad (i = 1, 2) \tag{10}$$

The following series representation of $1/r_{12}$ in terms of Legendre polynomials is well known (Flügge, 1974, Vol. 2, p. 63; McQuarrie, 1983, p. 340):

$$\frac{1}{r_{12}} = \sum_{l=0}^{+\infty} \frac{r_<^1}{r_>^{l+1}} P_l(s_1) \; P_l(s_2) \tag{11}$$

where $r_< = \min\{r_1, r_2\}$ and $r_> = \max\{r_1, r_2\}$.

Using (7), (11), the orthogonality of Legendre polynomials, and the useful formulas

$$\int_a^{+\infty} xe^{-\alpha x} \, dx = \left(\frac{1}{\alpha^2} + \frac{a}{\alpha}\right) e^{-\alpha a}$$

$$\int_0^b x^2 e^{-\alpha x} \, dx = \frac{2}{\alpha^3} - \left(\frac{2}{\alpha^3} + \frac{2b}{\alpha^2} + \frac{b^2}{\alpha}\right) e^{-\alpha b}.$$

$$\int_a^{+\infty} x^2 e^{-\alpha x} \, dx = \left(\frac{2}{\alpha^3} + \frac{2a}{\alpha^2} + \frac{a^2}{\alpha}\right) e^{-\alpha a}$$

$$\int_0^b x^3 e^{-\alpha x} \, dx = \frac{6}{\alpha^4} - \left(\frac{6}{\alpha^4} + \frac{6b}{\alpha^3} + \frac{3b^2}{\alpha^2} + \frac{b^3}{\alpha}\right) e^{-\alpha b}$$

$$\int_a^{+\infty} x^3 e^{-\alpha \mathrm{x}} \, dx = \left(\frac{6}{\alpha^4} + \frac{6a}{\alpha^3} + \frac{3a^2}{\alpha^2} + \frac{a^3}{\alpha}\right) e^{-\alpha a}$$

$$\int_0^b x^4 e^{-\alpha x}\,dx = \frac{24}{\alpha^5} - \left(\frac{24}{\alpha^5} + \frac{24b}{\alpha^4} + \frac{12b^2}{\alpha^3} + \frac{4b^3}{\alpha^2} + \frac{b^4}{\alpha}\right)e^{-ab}$$

we get

$$\begin{aligned}
&\langle\psi \frac{1}{r_{12}}\psi\rangle \\
&= \int_0^{+\infty}\int_{-1}^{+1}\int_0^{2\pi}\int_0^{+\infty}\int_{-1}^{+1}\int_0^{2\pi} \psi^2(r_1, r_2) \sum_{l=0}^{+\infty} \frac{r_<^l}{r_>^{l+1}} P_l(s_1)P_l(s_2) \\
&\qquad \times r_1^2 r_2^2\, dr_1\, ds_1\, d\omega_1\, dr_2\, ds_2\, d\omega_2 \\
&= 4\pi^2 \int_0^{+\infty}\int_0^{+\infty} \psi^2(r_1, r_2)\, \frac{2}{r_>}\, r_1^2 r_2^2\, dr_1\, dr_2 \\
&= 8\pi^2 \int_0^{+\infty} \left[\frac{1}{r_1}\int_0^{r_1} \psi^2(r_1, r_2) r_2^2\, dr_2 + \int_{r_1}^{+\infty} \psi^2(r_1, r_2) r_2\, dr_2\right] r_1^2\, dr_1 \\
&= \frac{1}{32\mu}(10 + 12c + 63c^2) \qquad (12)
\end{aligned}$$

From (7), applying again (4), we get

$$\begin{aligned}
\langle\psi\psi\rangle &= \int_0^{+\infty}\int_{-1}^{+1}\int_0^{2\pi}\int_0^{+\infty}\int_{-1}^{+1}\int_0^{2\pi} \psi^2(r_1, r_2) r_1^2\, r_2^2 dr_1 ds_1 d\omega_1 dr_2 ds_2 d\omega_2 \\
&= 1 + 9c^2 \qquad (13)
\end{aligned}$$

Taking (1) into account, the mean energy is

$$\begin{aligned}
\langle E\rangle &= \frac{\langle\psi\hat{H}\psi\rangle}{\langle\psi\psi\rangle} \\
&= \Bigg[-\frac{1}{2}(\langle\psi\nabla_1^2\psi\rangle + \langle\psi\nabla_1^2\psi\rangle) \\
&\qquad -2(\langle\psi\frac{1}{r_1}\psi\rangle + \langle\psi\frac{1}{r_2}\psi\rangle) + \langle\psi\frac{1}{r_{12}}\psi\rangle \Bigg] \Big/ \langle\psi\psi\rangle \qquad (14)
\end{aligned}$$

and from (8)–(10), (12), and (13), we obtain

$$\langle E\rangle = \frac{1 + 21c^2}{4\mu^2(1 + 9c^2)} - \frac{54 - 12c + 513c^2}{32\mu(1 + 9c^2)} \qquad (15)$$

Introducing $\alpha = 1/\mu$, the mean energy $\langle E\rangle$ becomes a rational function depending on two variational parameters α and c. Looking for stationary points of $\langle E\rangle$, the system of equations

$$\frac{\partial\langle E\rangle}{\partial\alpha} = 0, \qquad \frac{\partial\langle E\rangle}{\partial c} = 0$$

gives

$$\alpha = \frac{54 - 12c + 513c^2}{16(1 + 21c^2)} = \frac{-6 + 27c + 54c^2}{96c} \tag{16}$$

The second equality implies

$$378c^4 - 837c^3 - 99c - 2 = 0.$$

It is easy to approximate the real roots of this polynomial in c. For instance, using the package MATHEMATICA, Version 2.1 (Wolfram, 1991), the necessary commands are:

```
math
f[c_]:=378★c∧4−837★c∧3—99★c—2
NSolve[f[c] ==0,c]
Quit
```

The output gives the two real roots

$$c = -0.020132404375\,3751, \qquad c = 2.2657577738586\,5$$

the other two roots being complex numbers. The first value, $c = -0.020132404$, gives the minimum value of $\langle E\rangle$. From (16) we obtain $\alpha = 3.37437$, and therefore $\mu = 1/\alpha = 0.296351$ bohr, and the minimum value of the mean energy (15) is

$$\min\langle E\rangle = -2.860394 \text{ a.u.} = -77.8359 \text{ eV}$$

Remark 1. From experimental point of view, there is a variety of results mentioned for the true value of the double ionization potential of the helium atom, i.e., the energy value needed to dissociate both electrons from the helium nucleus. Thus, the following experimental values have been mentioned: −78.6 eV (Messiah, 1964), −78.62 eV (Anderson, 1971), −78.8882 and −78.8932 eV (Harnwell and Livingood, 1961), −78.9832 eV (Born, 1969), −78.99673525 eV (Dean, 1992), −79.0 eV (Striganov and Sventitskii, 1968; Fano, 1969; Böhm, 1979), −79.0052 eV (Lide, 1996). Some experimental physicists (Fano, 1969; Böhm, 1979) consider the value −79.0 eV as a lower bound, or a *threshold* for the double ionization potential of the helium atom.

Remark 2. If the two electrons of the helium atom are assumed to be statistically independent, which is equivalent to taking $c = 0$, the probability wave function (7) becomes

$$\psi(r_1,r_2) = \psi_1(r_1)\psi(r_2) = \frac{1}{\sqrt{8\pi\mu^3}} e^{-r_1/(2\mu)} \frac{1}{\sqrt{8\pi\mu^3}} e^{-r_2/(2\mu)}$$

Going through the same steps as above, we obtain

$$\langle\psi\nabla_i^2\psi\rangle = -\frac{1}{4\mu^2}, \qquad \langle\psi\frac{1}{r_i}\psi\rangle = \frac{1}{2\mu} \qquad (i = 1, 2)\ \langle\psi\frac{1}{r_{12}}\psi\rangle = \frac{5}{16\mu}$$

and, introducing these expressions into (14), we get

$$\langle E\rangle = \frac{1}{4\mu^2} - \frac{27}{16\mu}$$

Using again $\alpha = 1/\mu$ and taking

$$\frac{\partial\langle E\rangle}{\partial\alpha} = 0$$

we get $\alpha = 27/8 = 3.375$, which gives $\mu = 1/\alpha = 0.2962962$ bohr and

$$\min\langle E\rangle = -2.84765625 \text{ a.u.} = -77.48928281 \text{ eV}$$

This last case, dealing with statistically independent electrons, is generally treated in textbooks. It gives the approximation −77.4893 eV for the ground energy of the helium atom. As seen before, the more general assumption that the electrons are statistically linearly dependent gave a better approximation, namely −77.8359 eV. Moreover, the two variational parameters from the expression (7) of the probability wave function ψ may be easily interpreted. Thus, $\mu = 0.296351$ bohr gives the mean radial distance of the electrons from the nucleus, whereas the correlation coefficient $c = -0.020132404$ shows the intensity of the statistical linear dependence between the two electrons. As the two electrons both have a negative electric charge, they repel each other and consequently it is normal to have a negative linear correlation coefficient that reflects such a behavior. Due to the approximation $\sqrt{1 + t} \approx 1 + t/2$ used in getting the probability wave function ψ from the joint probability density of the two electrons, a more accurate evaluation of the linear correlation coefficient between the two electrons of the helium atom would be

$$\rho = \frac{2c}{1 + 9c^2} = -0.040118463$$

where the denominator is the norm of the probability wave function $\langle\psi^2\rangle =$

$1 + 9c^2$. The difference of the two approximations obtained for the ground energy, namely (−77.4893 eV) − (−77.8359 eV) = 0.3466 eV, could be taken as an energy measure of the linear radial dependence between the two electrons of the helium atom, whereas the difference between −77.8359 eV and the experimental value −79.0 eV, namely 1.1641 eV, is an energy measure of the nonlinear dependence between the two electrons.

Remark 3. Referring to (7), let us notice that the probability wave function should by antisymmetric, as required by the Pauli exclusion principle. If σ_i is the spin variable of electron $i (i = 1, 2)$, let α and β be the spin eigenfunctions. The orthonormality conditions imply

$$\int d\sigma_i \alpha^*(\sigma_i)\alpha(\sigma_i) = \int d\sigma_i\, \beta^*(\sigma_i)\beta(\sigma_i) = 1 \qquad (i = 1, 2)$$

$$\int d\sigma_i \alpha^*(\sigma_i)\beta(\sigma_i) = \int d\sigma_i\, \alpha^*(\sigma_i)\beta^*(\sigma_i) = 0 \qquad (i = 1, 2)$$

because two electrons with the same spatial quantum numbers must have opposite spin. The antisymmetric probability wave function is

$$\Psi = \psi(r_1,r_2)[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)]$$

Taking the orthonormality conditions into account and the fact that

$$\Psi^* = \psi(r_1,r_2)[\alpha^*(\sigma_1)\beta^*(\sigma_2) - \alpha^*(\sigma_2)\beta^*(\sigma_1)]$$

we obtain

$$\begin{aligned}\langle\Psi^*\hat{H}\Psi\rangle &= \int dr_1\, dr_2\, d\sigma_1\, d\sigma_2 \Psi^*\hat{H}\Psi \\ &= \int dr_1\, dr_2\, \psi(r_1,r_2)\, \hat{H}\psi(r_1,r_2) = \langle\psi\hat{H}\psi\rangle\end{aligned}$$

because the Hamiltonian $\hat{H}$ does not depend on spin. Similarly,

$$\langle\Psi^*\Psi\rangle = \int dr_1\, dr_2\, d\sigma_1\, d\sigma_2 \Psi^*\Psi = \int dr_1\, dr_2\, \psi(r_1 r_2)^2 = \langle\psi^2\rangle$$

Thus, we obtain

$$\langle E\rangle = \frac{\langle\Psi^*\hat{H}\Psi\rangle}{\langle\Psi^*\Psi\rangle} = \frac{\langle\psi\hat{H}\psi\rangle}{\langle\psi^2\rangle}$$

The last ratio has been used to calculate min $\langle E\rangle$.

2.2. The Ground Energy Using Higher Order Radial Generalized Correlations

Let us take a probability wave function (6) that contains five generalized radial correlations, replacing (7), which contains only one linear radial correlation, by

$$\begin{aligned}\psi(r_1,r_2) = \frac{1}{8\pi\mu^3} e^{-(r_1+r_2)/(2\mu)} \Bigg\{ 1 &+ a\left[L_1^{(2)}\left(\frac{r_1}{\mu}\right) + L_1^{(2)}\left(\frac{r_2}{\mu}\right)\right] \\ &+ bL_1^{(2)}\left(\frac{r_1}{\mu}\right) L_1^{(2)}\left(\frac{r_2}{\mu}\right) + c\left[L_2^{(2)}\left(\frac{r_1}{\mu}\right) + L_2^{(2)}\left(\frac{r_2}{\mu}\right)\right] \\ &+ q\left[L_1^{(2)}\left(\frac{r_1}{\mu}\right) L_2^{(2)}\left(\frac{r_2}{\mu}\right) + L_2^{(2)}\left(\frac{r_1}{\mu}\right) L_1^{(2)}\left(\frac{r_2}{\mu}\right)\right] \\ &+ gL_2^{(2)}\left(\frac{r_1}{\mu}\right) L_2^{(2)}\left(\frac{r_2}{\mu}\right)\Bigg\}\end{aligned}$$

Appendix A contains a MATHEMATICA program that does in this more involved case what we did analytically in the previous simpler case that dealt with the probability wave function (7). We obtain in this case

$$\mu = 0.260945353 \text{ bohr}, \qquad a = -0.0857747,$$

$$b = -0.0149716 \qquad c = 0.0255457,$$

$$q = -0.0000732054, \qquad g = -0.00114415$$

$$\min\langle E\rangle = -2.8783 \text{ a.u.} = -78.32315 \text{ eV}$$

It may be seen that the value obtained for the ground energy is closer to the experimental threshold −79.0 eV.

2.3, The Ground Energy Using Radial and Angular Generalized Correlations

The dependence between the two electrons of the helium atom may be expressed not only in terms of radial correlations, but of angular correlations as well. Thus, let us take the probability wave function (6) of the form

$$\begin{aligned}&\psi(r_1,r_2,s_1s_2) \\ &= \frac{1}{8\pi\mu^3} e^{-(r_1+r_2)/(2\mu)} \Bigg\{ 1 + a\left[L_1^{(2)}\left(\frac{r_1}{\mu}\right) + L_1^{(2)}\left(\frac{r_2}{\mu}\right)\right]\end{aligned}$$

$$+ bL_1^{(2)}\left(\frac{r_1}{\mu}\right)L_1^{(2)}\left(\frac{r_2}{\mu}\right) + c\left[L_2^{(2)}\left(\frac{r_1}{\mu}\right) + L_2^{(2)}\left(\frac{r_2}{\mu}\right)\right]$$
$$\left. + gL_2^{(2)}\left(\frac{r_1}{\mu}\right)L_2^{(2)}\left(\frac{r_2}{\mu}\right) + fP_1(s_1)P_1(s_2)\right\} \qquad (17)$$

where $L_n^{(2)}$ is the second-order Laguerre polynomial of degree n, and P_l is the Legendre polynomial of degree l.

We use here the Laplacian

$$\nabla_i^2\psi = \frac{\partial^2\psi}{\partial r_i^2} - \frac{2}{r_i}\frac{\partial\psi}{\partial r_i} - \frac{2s_i}{r_i^2}\frac{\partial\psi}{\partial s_i} + \frac{1-s_i^2}{r_i^2}\frac{\partial^2\psi}{\partial s_i^2} \qquad (i = 1,2) \qquad (18)$$

and the series expansion

$$\frac{1}{r_{12}} = \sum_{l=0}^{+\infty}\frac{r_<^l}{r_>^{l+1}}P_l(\cos\theta_1)P_l(\cos\theta_2) = \sum_{l=0}^{+\infty}\frac{r_<^l}{r_>^{l+1}}P_l(s_1)P_l(s_2)$$

where

$$r_< = \min\{r_1,r_2\}, \qquad r_> = \max\{r_1,r_2\}, \qquad s_i = \cos\theta_i \qquad (i = 1,2)$$

Appendix B contains a MATHEMATICA program that finds the minimum mean energy min $\langle E\rangle$, the mean distance μ of the electrons from the nucleus, and the values of the generalized radial (a,b,c,g) and angular (f) correlations. Running the program interactively, we obtain

$$\mu = 0.269261 \text{ bohr}, \qquad a = -0.0703336,$$
$$b = -0.0174889, \qquad c = 0.0241668, \qquad g = -0.00116699,$$
$$f = -0.0455481, \qquad \min\langle E\rangle = -2.88134 \text{ a.u.}$$
$$= -78.40587154 \text{ eV}$$

The value of f shows that the linear angular correlation between θ_1 and θ_2 is not negligible and its inclusion into the probability wave function (17) has improved the corresponding approximation of the ground energy.

2.4. A Generalization of Hylleraas' Trial Function

Long ago, Hylleraas (1929) had the idea of using r_1, r_2, and r_{12} as basic variables in dealing with the two electrons of the helium atom instead of the Cartesian or spherical coordinates. As mentioned in Hylleraas (1963, p. 425):

> A systematic attack on the ground state problem of the Helium atom had been planned by Max Born in cooperation with a pupil, Dr. Biemüller, since Born

> himself had no preference for numerical work. However, the enterprise came to a stop by the failing health of Dr. Biemüller before his work became particularly useful . . . Professor Born first suggested to me that—as he said—I was the right one to go on with the Helium problem . . . One thing which I noticed fairly soon was that solutions must exist which depend only on three coordinates, instead of the full number of six, and these were the coordinates r_1, r_2, φ, defining the shape of the electron nucleus triangle, leaving the orientation in space out of interest.

But the angle φ between r_1 and r_2 may be obviously connected to the distance r_{12} between the two electrons, because

$$2r_1r_2 \cos \varphi = r_1^2 + r_2^2 - r_{12}^2.$$

According to Hylleraas (1963, p. 427), “What I really invented was rather $u = r_{12}$, together with the $s = r_1 + r_2$ and $t = -r_1 + r_2$, forming the triple s, t, u of which I am really proud . . . The triple is forever reserved for atomic research.”

Taking a trial function of the form (2) with the polynomial $P(r_1, r_2, r_{12}) = cr_{12}$, namely

$$\psi(r_1,r_2,r_{12}) = e^{-\alpha r_1} e^{-\alpha r_2} (1 + cr_{12}) \tag{19}$$

with the volume element $r_1\, r_2\, r_{12}\, dr_1\, dr_2\, dr_{12}$, and using only two variational parameters α and c, he obtained

$$\min\langle E\rangle = -2.89112 \text{ a.u.} = -78.672 \text{ eV}$$

a result which, as he mentioned (Hylleraas, 1963, p. 427), “was greatly admired and thought of as almost a proof of the validity of wave mechanics, also, in the strict numerical sense.” Hylleraas’ approach, based on the variation-perturbation method, was refined in numerous subsequent papers, taking more and more coefficients of the polynomial $P(r_1, r_2, r_{12})$ in (6) as variational parameters, culminating with the work done by Pekeris (1959), who obtained the value

$$\min\langle E\rangle = -2.903724375 \text{ a.u.} = -79.0149862 \text{ eV}$$

by solving a determinant of order 1078. In fact this theoretical approximation is smaller than the smallest experimental value (−79.00519 eV) mentioned in the literature (Lide, 1996, p. 10–214), slightly contradicting the variational theorem. Details on the computations made by Hylleraas and his followers may be found in Hylleraas (1929, 1963), Bethe and Salpeter (1957), and Kinoshita (1957). Summarizing their approach, McQuarrie (1983, p. 294) writes:

> Although these calculations do show that one can obtain essentially exact energies by using the variational method with r_{12} in the trial function explicitly, these

> calculations are quite difficult computationally and do not readily lend themselves to large atoms and molecules. Furthermore, [in following this line of thought] we have abandoned the orbital concept altogether. The orbital concept has been of great use to chemists and so the trend nowadays is to find the Hartree–Fock orbitals . . . and to correct these by perturbation theory.

Let us notice that the starting point of the Hartree–Fock procedure for helium atom consists in writing the two-electron wave function as a product of orbitals, i.e.,

$$\psi(r_1, r_2) = \psi_1(r_1)\, \psi_2(r_2) \tag{20}$$

which, according to our probabilistic model, is equivalent to taking a probability wave function (6) with all generalized correlation coefficients equal to zero, which means that the electrons are supposed to be statistically independent. Let us mention that back in 1929, Hylleraas did not give any probabilistic justification for his trial function (19). Remarkably enough, he chose an exponential distribution for the marginals of the joint probability density, perhaps without being aware of the statistical significance of his choice, and introduced the distance r_{12} between electrons as a measure of their correlation. Using a wave function of the form (19) or (2), or more generally (6), does not mean to abandon orbitals. It simply means to take *statistically dependent* orbitals into account instead of *statistically independent* ones as expressed by (20). It is said (McQuarrie, 1983, p. 293) that starting from (20) and applying perturbation theory, "it turns out that one reaches a limit [i.e. min $\langle E \rangle = -2.8617$ a.u. $= -77.87143572$ eV] which is the best value of the energy that can be obtained using a trial function of the form of a product of one-electron wave functions (20)." Or, we have seen that using orbitals with radial linear dependence (7), the simplest case of statistical dependence between electrons, we have directly obtained a comparable value, -77.8359 eV, for the ground energy, without applying perturbation theory, whereas taking higher order correlations between electrons into account, the corresponding theoretical values of the ground energy approach the experimental threshold -79.0 eV.

Let us start from Hylleraas' trial function (19), which takes the interelectron distance r_{12} as an indicator of the interdependence between the two electrons, and include also the linear radial correlation between electrons, as in (7), namely

$$\psi(r_1, r_2, r_{12}) = e^{-r_1/(2\mu)}\, e^{-r_2/(2\mu)} \left[1 + c r_{12} + b L_1^{(1)}\left(\frac{r_1}{\mu}\right) L_1^{(1)}\left(\frac{r_2}{\mu}\right) \right] \tag{21}$$

with the volume element $r_1\, r_2\, r_{12}\, dr_1\, dr_2\, dr_{12}$, where $L_1^{(1)}(x) = 2 - x$. Let us notice that the choice of the Laguerre polynomial $L_1^{(1)}$ is justified by the fact that the radial probability density is $r_i e^{-r_i/\mu}$, i.e., the density of the gamma distribution **G** $(1/\mu, 2)$. We take into account that with respect to the variables r_1, r_2 and r_{12} the Hamiltonian has the form

$$\hat{H} = -\frac{1}{2}\frac{\partial^2\psi}{\partial r_1^2} - \frac{1}{r_1}\frac{\partial\psi}{\partial r_1} - \frac{1}{2}\frac{\partial^2\psi}{\partial r_2^2} - \frac{1}{r_2}\frac{\partial\psi}{\partial r_2} - \frac{\partial^2\psi}{\partial r_{12}^2} - \frac{2}{r_{12}}\frac{\partial\psi}{\partial r_{12}}$$
$$- \frac{r_1^2 - r_2^2 + r_{12}^2}{2r_1r_{12}}\frac{\partial^2\psi}{\partial r_1\partial r_{12}} - \frac{r_2^2 - r_1^2 + r_{12}^2}{2r_2r_{12}}\frac{\partial^2\psi}{\partial r_2\partial r_{12}}$$
$$- \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{r_{12}}\right)\psi \qquad (22)$$

We obtain in this case

$$\mu = 0.279794 \text{ bohr}, \qquad c = 0.310042, \qquad b = -0.016188$$
$$\min\langle E\rangle = -2.89511 \text{ a.u.} = -78.7806 \text{ eV}$$

which is a very good result, obtained by using only three variational parameters.

The most surprising fact comes up when an impressive improvement is obtained by taking into account a second-order radial correlation as well. Thus, starting from the probability wave function

$$\psi(r_1, r_2, r_{12})$$
$$= e^{-r_1/(2\mu)}\, e^{-r_2/(2\mu)}\left\{1 + cr_{12} + bL_1^{(1)}\left(\frac{r_1}{\mu}\right)L_1^{(1)}\left(\frac{r_2}{\mu}\right)\right.$$
$$\left. + a\left[L_2^{(1)}\left(\frac{r_1}{\mu}\right) + L_2^{(1)}\left(\frac{r_2}{\mu}\right)\right]\right\} \qquad (23)$$

and using again the Hamiltonian (22), we obtain

$$\mu = 0.281424 \text{ bohr}, \qquad c = 0.281515, \qquad b = -0.0171302$$
$$a = 0.0204191, \qquad \min\langle E\rangle = -2.90252 \text{ a.u.} = -78.9822 \text{ eV}$$

using only four variational parameters. At the same time, the probability wave function (23) and its coefficients have a clear interpretation: the distance of each electron from the nucleus is exponentially distributed with the mean μ, which, taking the volume element into account, gives a gamma radial probability distribution with parameters μ and 2, and the coefficients $2c$, $2b$, $2a$ are the distance between the two electrons and the first- and second-order generalized correlation coefficients, respectively.

Appendix C gives the MATHEMATICA program which implements the computation of the ground energy for (23), a program which runs interactively in approximately 1 hr on a standard personal computer IBM PS/2, Model 55 SX, with only 8 MB RAM and 60 MB hard disk. Let us notice that after calculating

$$\min\langle E\rangle = \frac{\langle \psi \hat{H} \psi\rangle}{\langle \psi^2\rangle}$$

as a function of the variational parameters μ, c, b, and a, the last command in the program asks for the minimum value of $\langle E\rangle$. Such a command needs arbitrary starting values of the variables μ, c, b, a. It is reasonable to choose $\mu = 1$ bohr and $c = b = a = 0$, which means that we start from the first average orbit and initially assume that the two electrons are statistically independent. Minimizing the mean energy of the system, the two electrons prove to interact statistically, moving on average closer to the nucleus, as an interelectron repelling effect, with a negative first-order (linear) correlation and positive distance between them and radial second-order (quadratic) generalized correlations.

3. THE GROUND STATE OF THE LITHIUM ATOM

The lithium atom represents an interesting system, where the three electrons randomly moving around the nucleus do not belong to the same energy shell. A shell picture of the atom has been in force since the time of the old quantum theory. In fact Pauli's exclusion principle ("Two electrons cannot be in exactly the same state") emerged along with spin ("If the spatial quantum numbers are the same, then the two electrons must have opposite spin") to explain the picture before the coming of quantum mechanics. The energy shells were originally defined to be the quantized electron orbits of Bohr's model.

If we (wrongly!) allow all three electrons of the lithium atom to interact freely inside the same energy shell, let us take the probability wave function

$$\begin{aligned}
\psi(r_1, r_2, r_3, s_1, s_2, s_3) \\
&= \frac{1}{\sqrt{8\pi\mu^3}} e^{-r_1/(2\mu)} \frac{1}{\sqrt{8\pi\mu^3}} e^{-r_2/(2\mu)} \frac{1}{\sqrt{8\pi\mu^3}} e^{-r_3/(2\mu)} \\
&\quad \times \left[1 + b_3 L_1^{(2)}\left(\frac{r_1}{\mu}\right) L_1^{(2)}\left(\frac{r_2}{\mu}\right) + b_2 L_1^{(2)}\left(\frac{r_1}{\mu}\right) L_1^{(2)}\left(\frac{r_3}{\mu}\right) + b_1 L_1^{(2)}\left(\frac{r_2}{\mu}\right) L_1^{(2)}\left(\frac{r_3}{\mu}\right)\right. \\
&\quad \left. + f_3 P_1(s_1) P_1(s_2) + f_2 P_1(s_1) P_1(s_3) + f_1 P_1(s_2) P_1(s_3)\right] \qquad (24)
\end{aligned}$$

which is a direct generalization to three electrons of the probability wave function (17), with $a = c = g = 0$, where $s_i = \cos\theta_i$ ($i = 1,2$). Using the Hamiltonian

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - \left(\frac{3}{r_1} + \frac{3}{r_2} + \frac{3}{r_3}\right) + \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right) \tag{25}$$

with the Laplacian ∇_i^2 given by (18), for $i = 1,2,3$, and

$$\frac{1}{r_{ij}} = \sum_{l=0}^{+\infty} \frac{(\min\{r_i, r_j\})^l}{(\max\{r_i, r_j\})^{l+1}} P_l(s_i) P_l(s_j)$$

we obtain the values

$$\mu = 0.210549 \text{ bohr}, \qquad b_1 = b_2 = b_3 = -0.0138212$$

$$f_1 = f_2 = f_3 = -0.0380186$$

$$\min\langle E\rangle = -8.50913 \text{ a.u.} = -231.547 \text{ eV}$$

which is a much smaller value than the experimental value −203.48619 eV (Lide, 1996, p. 10-214), which contradicts the variational theorem. This result shows that, indeed, the three electrons of the lithium atom are not interacting freely inside the same energy shell. Also, if the electrons are supposed to be statistically independent inside the same energy shell, a supposition which is equivalent to taking $b_i = f_i = 0$ ($i = 1, 2, 3$) in (24), then we get $\min\langle E\rangle = -230.236$ eV, a value which is also much below the experimental value −203.48619 eV.

Therefore, let us take the structure of the lithium atom as consisting of two interdependent electrons in the first closed energy shell, at a mean radial distance μ from the nucleus, and an independent electron in the second, open energy shell, at a mean radial distance ν from the nucleus. Let us emphasize that the two shells are not rigidly separated; the old orbits from Bohr's planetary model of the atom correspond to the mean radial distances μ and ν mentioned above. Because there is interdependence between the two electrons of the first shell, the mean radial distance μ is kept undetermined, as a variational parameter, starting from the initial value $\mu = 1$ bohr (as we did for the helium atom in the previous section), whereas the valence electron is the only one in the second energy shell, whose mean radial distance is taken to be $\nu = 2$ bohr. The probability wave function which assumes a linear radial dependence between the two electrons of the closed energy shell, with the linear correlation coefficient $2c$, an undetermined mean radial distance μ of the closed shell from the nucleus (starting with the initial value $\mu = 1$ bohr), and an independent valence electron in the open shell at a mean radial distance $\nu = 2$ bohr from the nucleus, is

$$\psi(r_1,r_2,r_3) = \left\{ \frac{1}{\sqrt{8\pi\mu^3}} e^{-r_1/(2\mu)} \frac{1}{\sqrt{8\pi\mu^3}} e^{-r_2/(2\mu)} \times \left[1 + c\, L_1^{(2)}\left(\frac{r_1}{\mu}\right) L_1^{(2)}\left(\frac{r_2}{\mu}\right) \right] \right\} \frac{1}{\sqrt{8\pi\nu^3}} e^{-r_3/(2\nu)} \tag{26}$$

with $\nu = 2$ bohr, and $\mu < \nu$, where

$$L_1^{(2)}(x) = 3 - x \qquad (i = 1, 2)$$

and the volume element is

$$r_1^2 r_2^2 r_3^2\, dr_1\, dr_2\, dr_3\, ds_1\, ds_2\, ds_3\, d\omega_1\, d\omega_2\, d\omega_3$$

with $s_i = \cos\theta_i$ $(i = 1, 2, 3)$.

Using the Hamiltonian (25) with the Laplacian

$$\nabla_i^2 \psi = \frac{\partial^2\psi}{\partial r_i^2} + \frac{2}{r_i}\frac{\partial\psi}{\partial r_i} (i = 1, 2, 3) \tag{27}$$

we obtain the values

$$\mu = 0.18622 \text{ bohr}, \qquad c = -0.0122754$$

and

$$\min\langle E\rangle = -7.46071 \text{ a.u.} = -203.018 \text{ eV}$$

which is a value of the ground energy amazingly close to the experimental value -203.486 eV.

Appendix D contains a MATHEMATICA program for calculating $\min\langle E\rangle$, using the probability wave function (26).

Remark 4. Compared with the helium atom, the two electrons making up the closed energy shell of the lithium atom are influenced by the existence of the open shell in the sense that on average they move closer to the nucleus and their random behavior is more regular, being adequately described by a linear radial statistical interdependence.

Remark 5. The value of $\min\langle E\rangle$ has been calculated by introducing ψ given by (26) into

$$\langle E\rangle = \frac{\langle\psi\hat{H}\psi\rangle}{\langle\psi^2\rangle}$$

and minimizing this expression with respect to the variational parameters μ and c. The probability wave function (26) is not antisymmetric, as required by the Pauli exclusion principle. Let us denote

$$u(i, j) = \frac{1}{\sqrt{8\pi\mu^3}}\, e^{-r_i/(2\mu)}\, \frac{1}{\sqrt{8\pi\mu^3}}\, e^{-r_j/(2\mu)} \left[1 + cL_1^{(2)}\left(\frac{r_i}{\mu}\right) L_1^{(2)}\left(\frac{r_j}{\mu}\right)\right]$$

$$v(k) = \frac{1}{\sqrt{8\pi 2^3}}\, e^{-r_k/4}$$

for $i, j, k = 1, 2, 3$. If σ_i is the spin variable of electron i ($i = 1, 2, 3$), let α and β be the spin eigenfunctions of the electrons belonging to the closed energy shell and γ be the spin eigenfunction of the valence electron. We have the normality conditions

$$\int d\sigma_i\, \alpha^*(\sigma_i)\alpha(\sigma_i) = \int d\sigma_i\, \beta^*(\sigma_i)\beta(\sigma_i) = \int d\sigma_i\, \gamma^*(\sigma_i)\gamma(\sigma_i) = 1 \qquad (i = 1,2,3) \quad (28)$$

and the orthogonality conditions

$$\int d\sigma_i \alpha^*(\sigma_i)\beta(\sigma_i) = \int d\sigma_i \alpha(\sigma_i)\beta^*(\sigma_i) = \int d\sigma_i \alpha^*(\sigma_i)\gamma(\sigma_i) = \int d\sigma_i \alpha(\sigma_i)\gamma^*(\sigma_i) = \int d\sigma_i \beta^*(\sigma_i)\gamma(\sigma_i) = \int d\sigma_i\, \beta(\sigma_i)\gamma^*(\sigma_i) = 0 \quad (29)$$

for $i = 1, 2, 3$, because two electrons belonging to the closed energy shell cannot have the same spin and an electron cannot belong simultaneously both to the open energy shell and to the closed energy shell. The antisymmetric probability wave function corresponding to (26) is

$$\begin{aligned}\Psi &= u(1, 2)v(3)[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)]\gamma(\sigma_3) \\ &\quad -u(1, 3)v(2)[\alpha(\sigma_1)\beta(\sigma_3) - \beta(\sigma_1)\alpha(\sigma_3)]\gamma(\sigma_2) \\ &\quad +u(2, 3)v(1)[\alpha(\sigma_2)\beta(\sigma_3) - \beta(\sigma_2)\alpha(\sigma_3)]\gamma(\sigma_1) \qquad (30) \\ &= \begin{vmatrix} \alpha(\sigma_1) & \beta(\sigma_1) & u(2, 3)v(1)\gamma(\sigma_1) \\ \alpha(\sigma_2) & \beta(\sigma_2) & u(1, 3)v(2)\gamma(\sigma_2) \\ \alpha(\sigma_3) & \beta(\sigma_3) & u(1, 2)v(3)\gamma(\sigma_3) \end{vmatrix}\end{aligned}$$

Taking into account the orthonormality conditions (28), (29), and the fact that

$$\begin{aligned}\Psi^* = {} & u(1,2)v(3)[\alpha^*(\sigma_1)\beta^*(\sigma_2) - \beta^*(\sigma_1)\alpha^*(\sigma_2)]\gamma^*(\sigma_3)\\ & - u(1,3)v(2)[\alpha^*(\sigma_1)\beta^*(\sigma_3) - \beta^*(\sigma_1)\alpha^*(\sigma_3)]\gamma^*(\sigma_2)\\ & + u(2,3)v(1)[\alpha^*(\sigma_2)\beta^*(\sigma_3) - \beta^*(\sigma_2)\alpha^*(\sigma_3)]\gamma^*(\sigma_1)\end{aligned}$$

we obtain

$$\begin{aligned}\langle \Psi^* \hat{H} \Psi \rangle &= \int dr_1\, dr_2\, dr_3\, d\sigma_1\, d\sigma_2\, d\sigma_3\; \Psi^* \hat{H}\, \Psi\\ &= 2 \int dr_1\, dr_2\, dr_3\; u(1,2)v(3)\hat{H}u(1,2)v(3)\\ &\quad +2 \int dr_1\, dr_2\, dr_3\; u(2,3)v(1)\hat{H}u(2,3)v(1)\\ &\quad +2 \int dr_1\, dr_2\, dr_3\; u(1,3)v(2)\hat{H}u(1,3)v(2)\end{aligned}$$

because the Hamiltonian $\hat{H}$ does not depend on spin. As $\hat{H}$ is symmetric, we get

$$\langle \Psi^* \hat{H} \Psi \rangle = 6 \int dr_1\, dr_2\, dr_3\; u(1,2)v(3)\hat{H}u(1,2)v(3) = 6\langle \psi \hat{H} \psi \rangle$$

Similarly, we get

$$\begin{aligned}\langle \Psi^* \Psi \rangle &= \int dr_1\, dr_2\, dr_3\, d\sigma_1\, d\sigma_2\, d\sigma_3\; \Psi^* \Psi\\ &= 6 \int dr_1\, dr_2\, dr_3\; [u(1,2)v(3)]^2 = 6\langle \psi^2 \rangle\end{aligned}$$

Thus, we finally get

$$\langle E \rangle = \frac{\langle \Psi^* \hat{H} \Psi \rangle}{\langle \Psi^* \Psi \rangle} = \frac{\langle \psi \hat{H} \psi \rangle}{\langle \psi^2 \rangle}$$

as used by us to calculate $\min\langle E \rangle$.

4. CONCLUSION

In standard nonrelativistic quantum mechanics, the Schrödinger equation is taken as a postulate and the squared absolute value of its solution is interpreted as being a probability density function used for making predictions about the behavior of quantum systems. This paper deals with a nonstandard approach. Given a quantum system, we determine the probability wave function whose corresponding probability distribution (i.e., the square of its absolute value) is the closest one to statistical equilibrium subject to generalized correlation coefficients whose values are obtained by looking for the stationary points of the mean energy of the system. Statistical equilibrium, determined by using the principle of maximum entropy, gives the most unbiased probability distribution on the possible states of the system subject to given mean values. The closest probability distribution to statistical equilibrium is obtained by minimizing Pearson's mean deviation subject to given generalized correlation coefficients whose values are obtained, as said before, by looking for stationary points of the mean energy of the system. This paper uses this principle of minimum mean deviation from statistical equilibrium as a tool for constructing a mathematical model that allows simple approximations for the ground state of the helium and lithium atoms, while keeping the computation relatively simple. The advantage of this tool consists mainly in its flexibility in dealing with interdependent particles. According to McQuarrie (1983, p. 297), "the inclusion of electron correlations in atomic and molecular wave functions is a problem of current and active interest."

APPENDIX A

We use MATHEMATICA, Version 2.1 (Wolfram, 1991), including the subroutine ‘integExp‘ from the package ”Quantum” (Feagin, 1994). If the fast subroutine ‘integExp‘ is not available, then the command Integrate may be used instead. In the program below, in order to simplify the writing, x, y, m, and ppsi[x,y] are the symbols replacing r_1, r_2, μ, and $\psi(r_1\ r_2)$, respectively. At the end of each line press the Enter key.

```
math
Needs [”Quantum ‘integExp‘ ”]
psi[x_]:=((8★(m^3)★Pi)^(−1/2))★ Exp[−x/(2★m)]
ppsi[x_,y_]:=psi[x]★psi[y]★(1+a★(LaguerreL[1,2,x/m]+
LaguerreL[1,2,y/m])+b★LaguerreL[1,2,x/m]★LaguerreL[1,2,y/m]+
c★(LaguerreL[2,2,x/m]+LaguerreL[2,2,y/m])+
q★(LaguerreL[1,2,x/m]★LaguerreL[2,2,y/m]+
LaguerreL[2,2,x/m]★LaguerreL[1,2,y/m])+
g★LaguerreL[2,2,x/m]★LaguerreL[2,2,y/m])
Expand[16★Pi^2★x^2★y^2★ppsi[x,y]^2]
integExp[%,{x,0,Infinity}]
integExp[%,{y,0,Infinity}]
Expand[16★Pi^2★x^2★y^2★ ppsi[x,y]★
(D[ppsi[x,y],{x,2}]+2★D[ppsi[x,y],x]/x)]
integExp[%,{x,0,Infinity}]
```

```
integExp[%,{y,0,Infinity}]
Expand[16★Pi^2★x^2★y^2★ ppsi[x,y]★
(D[ppsi[x,y],{y,2}]+2★D[ppsi[x,y],y]/y)]
integExp[%,{y,0,Infinity}]
integExp[%,{x,0,Infinity}]
Expand [16★Pi^2★x^2★y^2★ (ppsi[x,y]^2)/x]
integExp[%,{x,0,Infinity}]
integExp[%,{y,0,Infinity}]
Expand [16★Pi^2★x^2★y^2★ (ppsi[x,y]^2)/y]
integExp[%,{y,0,Infinity}]
integExp[%,{x,0,Infinity}]
Expand[(ppsi[x,y]/psi[x])^2★y★(y−x)]
Integrate[%,{y,0,x}]
Expand[(ppsi[x,y]/psi[x])^2★y]
integExp[%,{y,0,Infinity}]
x★(%%%+x★%)
Expand [16★Pi^2★psi[x]^2★%]
integExp[%,{x,0,Infinity}]
−(%%%%%%%%%%%%%%%%%+%%%%%%%%%%%%%%)/2
−2★(%%%%%%%%%%%%+%%%%%%%%%)
(%%+%+%%%)/ %%%%%%%%%%%%%%%%%%%%%%
Find Minimum [%,{m,1},{a,0},{b,0},{c,0},{q,0} ,{g,0}]
Quit
```

APPENDIX B

We use MATHEMATICA, Version 2.1 (Wolfram, 1991), including the subroutine ‘integExp‘ from the package ”Quantum” (Feagin, 1994). If the fast subroutine ‘integExp‘ is not available, then the command Integrate may be used instead. In the program below, in order to simplify the writing, x, y, m, u, v, and ppsi[x,y,u,v] are the symbols replacing r_1, r_2, μ, s_1, s_2, and $\psi(r_1, r_2, s_1, s_2)$), respectively. At the end of each line press the Enter key.

```
math
Needs [”Quantum‘integExp‘ ”]
psi[x_]:=((8★(m^3)★Pi)^(−1/2))★Exp[−x/(2★m)]
ppsi[x_,y_,u_,v_]:=psi[x]★psi[y]★(1+a★(LaguerreL[1,2,x/m]+
LaguerreL[1,2,y/m])+b★LaguerreL[1,2,x/m]★LaguerreL[1,2,y/m]+
c★(LaguerreL[2,2,x/m]+LaguerreL[2,2,y/m])+
g★LaguerreL[2,2,x/m]★LaguerreL[2,2,y/m])+
f★LegendreP[1,u]★LegendreP[1,v])
Expand[4★Pi^2★x^2★ppsi[x,y,u,v] ^2]
```

```
integExp[%,{x,0,Infinity}]
integExp[y^2★%,{y,0,Infinity}]
Integrate[%,{u,−1,1},{v,−1,1}]
laplace[x_,y_,u_,v_]:=D[ppsi[x,y,u,v],{x,2}]+
2★D[ppsi[x,y,u,v],x]/x−2★u★D[ppsi[x,y,u,v,],u]/(x^2)
Expand[4★Pi^2★x^2★ppsi[x,y,u,v] ★ laplace[x,y,u,v]]
integExp[%,{x,0,Infinity}]
integExp[y^2★%,{y,0,Infinity}]
Integrate[%,{u,−1,1},{v,−1,1}]
integExp[4★Pi^2★x★ppsi[x,y,u,v]^2,{x,0,Infinity}]
integExp[y^2★%,{y,0,Infinity}]
Integrate[%,{u,−1,1},{v,−1,1}]
Expand[(1/x −1/y+(y/x^2−x/y^2)★u★v)★ (ppsi[x,y,u,v]/
(psi[x]★psi[y]))^2]
Integrate[%,{u,−1,1},{v,−1,1}]
Expand[%★y^2★psi[y]^2★(2★Pi)]
Integrate[%,{y,0,x}]
Expand[(1/y +(x/y^2)★u★v)★(ppsi[x,y,u,v]/ (psi[x]★psi[y]))^2]
Integrate[%,{u,−1,1},{v,−1,1}]
Expand[%★y^2★psi[y]^2★(2★Pi)]
integExp[%,{y,0,Infinity}]
%%%%%+%
integExp[%★x^2★psi[x]^2★(2★Pi),{x,0,Infinity}]
−%%%%%%%%%%%%%%−4★%%%%%%%%%%%+%
FindMinimum[%,{m,1},{a,0},{b,0},{c,0},{g,0} ,{ f,0}]
Quit
```

APPENDIX C

We use MATHEMATICA, Version 2.1 (Wolfram, 1991), including the subroutine ‘integExp‘ from the package ”Quantum” (Feagin, 1994). If the fast subroutine ‘integExp‘ is not available, then the command Integrate may be used instead. In the program below, in order to simplify the writing, x, y, z, ppsi[x,y,z], m, and hamppsi are the symbols replacing r_1, r_2, r_{12}, $\psi(r_1, r_2, r_{12})$, μ, and $\hat{H}\,\psi$, respectively. At the end of each line press the Enter key.

```
math
Needs[”Quantum‘integExp‘ ”]
ppsi[x_,y_,z_]:=Exp[−(x+y)/(2★m)]★(1+c★z+
b★LaguerreL[1,1,x/m]★LaguerreL[1,1,y/m]+
a★(LaguerreL[2,1,x/m]+LaguerreL[2,1,y/m]))
hamppsi[x_,y_,z_]:=−D[ppsi[x,y,z],{x,2}]/2−
```

```
D[ppsi[x,y,z],x]/x−D[ppsi[x,y,z],{y,2}]/2−
D[ppsi[x,y,z],y]/y−D[ppsi[x,y,z],{z,2}]−
2★D[ppsi[x,y,z],z]/z−(x^2−y^2+z^2)★
D[D[ppsi[x,y,z],x],z]/(2★x★z)− (y^2−x^2+z^2)★
D[D[ppsi[x,y,z],y],z]/(2★y★z)− (2/x+2/y−1/z)★ppsi[x,y,z]
Expand[ppsi[ x,y,z]★hamppsi[x,y,z] ★x★y★z]
Integrate[%,{z,x−y,x+y}]
Integrate[%,{y,0,x}]
integExp[%,{x,0,Infinity}]
Integrate[%%%%,{z,y−x,x+y}]
integExp[%,{y,0,Infinity}]
Integrate[%%,{y,0,x}]
%%−%
integExp[%,{x,0,Infinity}]
%%%%%%+%
Expand[ppsi[ x,y,z,]^2★x★y★z]
Integrate[%,{z,x−y,x+y}]
Integrate[%,{y,0,x}]
integExp[%,{x,0,Infinity}]
Integrate[%%%%,{z,y−x,x+y}]
integExp[%,{y,0,Infinity}]
Integrate[%%,{y,0,x}]
%%−%
integExp[%,{x,0,Infinity}]
%%%%%%+%
%/%%
FindMinimum[%,{m,1},{c,0},{b,0},{a,0}]
Quit
```

APPENDIX D

We use MATHEMATICA, Version 2.1 (Wolfram, 1991), including the subroutine ‘integExp‘ from the package ”Quantum” (Feagin, 1994). If the fast subroutine ‘integExp‘ is not available, then the command Integrate may be used instead. The program below starts from the probability wave function (26), with the Hamiltonian (25), for which the Laplacian is (27). In order to simplify the writing, x, y, z, m, ppsi[x,y], and hamppsi are the symbols replacing r_1, r_2, r_3, μ, ψ (r_1, r_2, r_3), and $\hat{H}\psi$, respectively. At the end of each line press the Enter key.

```
math
Needs [”Quantum‘integExp‘ ”]
```

```
psi[x_]:=((8★(m^3)★Pi)^(−1/2))★Exp[−x/(2★m)]
qsi[z_]:=((8★2^3★Pi)^(−1/2))★Exp[−z/(2★2)]
ppsi[x_,y_,z_]:=psi[x]★psi[y]★(1+c★LaguerreL[1,2,x/m]★
LaguerreL[1,2,y/m])★qsi[z]
integExp[8★Pi^3★x★ppsi[x,y,z]^2, {x,0,Infinity}]
integExp[y^2★%,{y,0,Infinity}]
integExp[z^2★%,{z,0,Infinity}]
Together[%]
integExp[8★Pi^3★z★ppsi[x,y,z] ^2, {z,0,Infinity}]
integExp[x^2★%,{x,0,Infinity}]
integExp[y^2★%,{y,0,Infinity}]
6★%%%%%+3★%
laplace1[x_,y_,z_]:=D[ppsi[x,y,z],{x,2}]+2★D[ppsi[x,y,z],x]/x
Expand[8★Pi^3★x^2★ppsi[x,y,z] ★laplace1[x,y,z]]
integExp[%,{x,0,Infinity}]
integExp[y^2★%,{y,0,Infinity}]
integExp[z^2★%,{z,0,Infinity}]
laplace3[x_,y_,z_]:=D[ppsi[x,y,z],{z,2}]+2★D[ppsi[x,y,z],z]/z
Expand[8★Pi^3★z^2★ppsi[x,y,z] ★laplace3[x,y,z]]
integExp[%,{z,0,Infinity}]
integExp[x^2★%,{x,0,Infinity}]
integExp[y^2★%,{y,0,Infinity}]
−%%%%%%%−%/2−%%%%%%%%%%%%%
t12[x_,y_,z_]:=ppsi[x,y,z]/psi[x]
Expand[4★Pi^2★z^2★t12[x,y,z,] ^2]
integExp[%,{z,0,Infinity}]
Expand[%★y★(y−x)]
Integrate[%,{y,0,x}]
Expand[%%%★y]
integExp[%,{y,0,Infinity}]
x★(%%%+x★%)
Expand[2★Pi★psi[x]^2★%]
integExp[%,{x,0,Infinity}]
t23[x_,y_,z_]:=ppsi[x,y,z]/psi[y]
Expand[4★Pi^2★x^2★t23[x,y,z]^2]
integExp[%,{x,0,Infinity}]
Expand[%★z★(z−y)]
Integrate[%,{z,0,y}]
Expand[%%%★z]
integExp[%,{z,0,Infinity}]
y★(%%%+y★%)
Expand[2★Pi★psi[y]^2★%]
```

```
integExp[%,{y,0,Infinity}]
%%%%%%%%%%%%%%%%%%%%%%%
%+%%%%%%%%%%%%%+2★%%
integExp[8★Pi^3★x^2★ppsi[x,y,z]^2, {x,0,Infinity}]
integExp[y^2★%,{y,0,Infinity}]
integExp[z^2★%,{z,0,Infinity}]
%%%%%/%
FindMinimum[%,{m,1},{c,0}]
Quit
```

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