AN EXERCISE ON THE EVALUATION OF AVERAGE VALUES OF OBSERVABLES

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An useful exercise which can be proposed to students involved in elementary quantum chemistry is the calculation of average values of observables, with the aim to make the study of the theoretical chemistry less abstract and students more familiar with actual calculations of quantum integrals. Moreover, a suitable choice of the average values to be calculated can help to get more insight in important concepts of quantum chemistry, like the Heisenberg uncertainty principle.

It is opportune to propose some examples where the wavefunction is simple enough to easily calculate the average values.

Let us take, as a first example, the particle in a monodimensional box of length a, whose real wavefunction is
$\psi_k = (2/a)^{1/2}\sin(kx)$
with $k = n\pi/a$, $n = 1,2,3,...$[1]

Let us calculate the average values of x, x^2, p_x and p_x^2, that is the integrals :
$\langle x\rangle = \langle\psi_k|x|\psi_k\rangle$, $\langle x^2\rangle = \langle\psi_k|x^2|\psi_k\rangle$,
$\langle p_x\rangle = \langle\psi_k|-i\hbar d/dx|\psi_k\rangle$,
$\langle p_x^2\rangle = \langle\psi_k|-\hbar^2 d^2/dx^2|\psi_k\rangle$.
$\langle x\rangle = \langle\psi_k|x|\psi_k\rangle = (2/a)\int_0^a x\sin^2(kx)dx$.

Making the change of variable kx = t,
$\langle x\rangle = (2/ak^2)\int_0^{ka} t\sin^2 t\,dt$.

The indefinite integral of $t\sin^2 t$ is the function $t^2/4 - t\sin(2t)/4 - \cos(2t)/8$ [2], and remembering that $ka = n\pi$,
we obtain $\langle x\rangle = (2/ak^2)(k^2a^2)/4 = a/2$.
$\langle x^2\rangle = \langle\psi_k|x^2|\psi_k\rangle = (2/a)\int_0^a x^2\sin^2(kx)dx =$
$= (2/ak^3)\int_0^{ka} t^2\sin^2 t\,dt$.

Being the integral of $t^2\sin^2 t$ the function $t^3/6 - (t^2/4 - 1/8)\sin(2t) + -t\cos(2t)/4$ [2], we obtain
$\langle x^2\rangle = (2/ak^3)(k^3a^3/6 - ka/4) =$
$= a^2/3 - 1/2k^2 = a^2(1/3 - 1/2n^2\pi^2)$.

$\langle p_x\rangle = \langle\psi_k|(-i\hbar d/dx|\psi_k\rangle = (2/a)(-i\hbar)$
$\int_0^a \sin(kx)k\cos(kx)dx = (-2i\hbar/a)$
$\int_0^{ka} \sin t\cos t\,dt = (-2i\hbar/a)[\sin^2 t/2]_0^{n\pi}\pi = 0$.

This result is to be expected on the basis of the following considerations. Since $\langle p_x\rangle$, corresponding to an average value of a physical observable, is a real value, the integral $\langle\psi_k|p_x|\psi_k\rangle$ must be zero, because of the presence of the imaginary constant. Moreover, simple considerations on the symmetry properties of the integrand lead to the same result.

$\langle p_x^2\rangle = \langle\psi_k|(-\hbar^2 d^2/dx^2|\psi_k\rangle =$
$= (-2\hbar^2/a)\int_0^a -k^2\sin^2(kx)dx =$
$= (2\hbar^2 k/a)\int_0^{ka} \sin^2 t\,dt =$
$= (2\hbar^2 k/a)[t/2 - \sin(2t)/4]_0^{ka} =$
$= (2\hbar^2 k/a)ka/2 = (n\hbar\pi/a)^2$.

It is possible to obtain the same result for $\langle p_x^2\rangle$ operating with p_x^2 on the wavefunction and identifying the eigenvalue with the average value, being the wavefunction eigenfunction of this operator.

Alternatively, remembering that in this case $\langle p_x^2\rangle = 2mE$, given the energy of the particle $n^2h^2/8ma^2$, $\langle p_x^2\rangle = (n\hbar\pi/a)^2$.

As further exercise, it is possible to verify that the Heisenberg principle holds, that is $\Delta x\Delta p_x \geq |\langle C\rangle|/2$, where $\Delta x = (\langle x^2\rangle - \langle x\rangle^2)^{1/2}$, $\Delta p_x = (\langle p_x^2\rangle - \langle p_x\rangle^2)^{1/2}$ and $|\langle C\rangle| = |\langle\psi|i[x,p_x]|\psi\rangle| = \hbar$.

Now,
$\Delta x = \{a^2(1/3 - 1/2n^2\pi^2) - a^2/4\}^{1/2} =$
$= a(1/12 - 1/2n^2\pi^2)^{1/2}$. $\Delta p_x = n\hbar\pi/a$.
$\Delta x\Delta p_x = n\hbar\pi(1/12 - 1/2n^2\pi^2)^{1/2} =$
$= (\hbar/2)(n^2\pi^2/3 - 2)^{1/2}$
to be compared with $|\langle C\rangle| = \hbar/2$.

For n = 1, $\Delta x\Delta p_x = (\hbar/2)(\pi^2/3 - 2)^{1/2}$ which is slightly larger than $\hbar/2$, in accord with the Heisenberg principle. The values of $\Delta x\Delta p_x$ increase approximately linearly with n.

As a second example, we consider the wavefunctions of the hydrogen atom and calculate, as above, the values of $\langle x\rangle$, $\langle x^2\rangle$, $\langle p_x\rangle$ and $\langle p_x^2\rangle$.

Let us consider the 1s wavefunction. $1s = (\pi a_0^3)^{-1/2}\exp(-r/a_0)$ where a_0 is the Bohr radius $= \hbar^2/m_e e^2$.
$\langle x\rangle = \langle 1s|x|1s\rangle = \iiint(\pi a_0^3)^{-1/2}\exp(-r/a_0)\,x\,(\pi a_0^3)^{-1/2}\exp(-r/a_0)r^2 dr\sin\theta d\theta d\varphi =$
$= (\pi a_0^3)^{-1}\iiint\exp(-2r/a_0)(r\sin\theta\cos\varphi)\,r^2 dr\sin\theta d\theta d\varphi$.

Since the integral on the φ coordinate is $\int_0^{2\pi}\cos\varphi d\varphi = 0$, $\langle x\rangle = 0$.

Also in this case simple considerations about the symmetry properties of the integrand lead to a null value of the integral.
$\langle x^2\rangle = \langle 1s|x^2|1s\rangle =$
$= \iiint(\pi a_0^3)^{-1/2}\exp(-r/a_0)x^2(\pi a_0^3)^{-1/2}\exp(-r/a_0)r^2 dr\sin\theta d\theta d\varphi =$
$= (\pi a_0^3)^{-1}\iiint\exp(-2r/a_0)(r\sin\theta\cos\varphi)^2 r^2 dr\sin\theta d\theta d\varphi = (\pi a_0^3)^{-1}(\int_0^\infty\exp(-2r/a_0)r^4 dr \int_0^\pi \sin^3\theta d\theta \int_0^{2\pi}\cos^2\varphi d\varphi)$.

We have to solve separately the three integrals on the coordinates r, θ and φ.
$\int_0^\pi \sin^3\theta d\theta = [-\cos\theta(\sin^2\theta + 2)/3]_0^\pi =$
$= 4/3$. [3]
$\int_0^{2\pi}\cos^2\varphi d\varphi = [\varphi/2 + (\sin 2\varphi)/4]_0^{2\pi} =$
$= \pi$. [3]

Making the change of variable $2r/a_0 = t$,
$\int_0^\infty \exp(-2r/a_0)r^4 dr =$
$= (a_0/2)^5\int_0^\infty \exp(-t)t^4 dt$. $\int_0^\infty \exp(-t)t^4 dt =$
$= [-\exp(-t)t^4]_0^\infty + 4\int_0^\infty \exp(-t)t^3 dt =$
$= 4([-\exp(-t)t^3]_0^\infty + 3\int_0^\infty \exp(-t)t^2 dt) =$
$= 12([-\exp(-t)t^2]_0^\infty + 2\int_0^\infty \exp(-t)t\,dt) =$
$= 24[-\exp(-t)]_0^\infty = 24$.

Finally, $\langle x^2\rangle = (\pi a_0^3)^{-1}(a_0/2)^5\,24\,(4/3)\pi = a_0^2$.
$\langle p_x\rangle = (\pi a_0^3)^{-1}\iiint\exp(-r/a_0)(-i\hbar\partial/\partial x)\exp(-r/a_0)r^2 dr\sin\theta d\theta d\varphi =$
$= (-i\hbar)(\pi a_0^3)^{-1}\iiint\exp(-r/a_0)(\partial/\partial x)(\exp(-(x^2 + y^2 + z^2)^{1/2}/a_0))r^2 dr\sin\theta d\theta d\varphi =$
$= (-i\hbar)(\pi a_0^3)^{-1}\iiint\exp(-r/a_0)(-\exp(-(x^2 + y^2 + z^2)^{1/2}/a_0))(1/a_0)(1/2(x^2 + y^2 + z^2)^{1/2})2x\,r^2 dr\sin\theta d\theta d\varphi = (-i\hbar)(\pi a_0^4)^{-1}\iiint\exp(-2r/a_0)(1/r)r\sin\theta\cos\varphi\,r^2 dr\sin\theta d\theta d\varphi$.

Since the integral on the φ coordinate is $\int_0^\pi \cos\varphi d\varphi = 0$, $\langle p_x\rangle = 0$.

Also in this case simple considerations about the symmetry properties of the integrand give the result above.
$\langle p_x^2\rangle = (-\hbar^2)(\pi a_0^3)^{-1}\iiint\exp(-r/a_0)(\partial^2/\partial x^2)(\exp(-(x^2 + y^2 + z^2)^{1/2}/$

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$a_0))r^2 dr \sin\theta d\theta d\varphi =$
$= (-\hbar^2)(\pi a_0^3)^{-1}\iiint \exp(-r/a_0)(\partial/\partial x)(-\exp(-r/a_0)(x/ra_0))r^2 dr \sin\theta d\theta d\varphi =$
$= \hbar^2(\pi a_0^4)^{-1}\iiint \exp(-r/a_0)\{(-\exp(-r/a_0))(1/a_0)(x/r)(x/r) + \exp(-r/a_0)(r - x^2/r)/r^2\}r^2 dr \sin\theta d\theta d\varphi = \hbar^2(\pi a_0^4)^{-1}\iiint \exp(-2r/a_0)(-x^2/a_0 r^2 + 1/r - x^2/r^3)r^2 dr \sin\theta d\theta d\varphi =$
$= \hbar^2(\pi a_0^4)^{-1}\{(-1/a_0)\int_0^\infty \exp(-2r/a_0)r^2 dr \int_0^\pi \sin^3\theta d\theta \int_0^{2\pi} \cos^2\varphi d\varphi +$
$+ \int_0^\infty \exp(-2r/a_0) r dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi +$
$-\int_0^\infty \exp(-2r/a_0) r dr \int_0^\pi \sin^3\theta d\theta \int_0^{2\pi} \cos^2\varphi d\varphi\}.$

As shown above in the case of the calculation of $\langle x^2\rangle$,
$\int_0^\infty \exp(-2r/a_0)r^2 dr = (a_0/2)^3\int_0^\infty \exp(-t)t^2 dt = 2(a_0/2)^3 = a_0^3/4.$
$\int_0^\infty \exp(-2r/a_0) r dr = (a_0/2)^2.$
$\int_0^\pi \sin^3\theta d\theta = 4/3. \int_0^{2\pi} \cos^2\varphi d\varphi = \pi.$
Moreover, $\int_0^{2\pi} d\varphi = 2\pi$ and $\int_0^\pi \sin\theta d\theta = 2$.
Finally, we obtain
$\langle p_x\rangle = \hbar^2(\pi a_0^4)^{-1}\{(-1/a_0)(a_0^3/4)(4\pi/3) + (a_0^2/4)4\pi - (a_0^2/4)(4\pi/3)\} =$
$= (\hbar^2/a_0^4)(-a_0^2/3 + a_0^2 - a_0^2/3) = \hbar^2/3a_0^2.$

As in the previous example, the Heisenberg principle can be easily verified.

$\Delta x\Delta p_x = (a_0^2\hbar^2/3a_0^2)^{1/2} = \hbar/\sqrt{3}$ to be compared with $|\langle C\rangle|/2 = \hbar/2$; since $\sqrt{3}$ is smaller than 2, it is verified that $\Delta x\Delta p_x > |\langle C\rangle|/2$.

Analogous results can be obtained for the other wavefunctions of the hydrogen atom, keeping in mind that, when functions with quantum number $l>0$ are considered, different values for x, y and z coordinates can be obtained. The results for the 1s, 2s, 2p, 3s, 3p and $3d_0$ functions are reported in the Table below.

The $\langle z^2\rangle/\langle x^2\rangle$ ratio, r, depends on the quantum numbers l and $|m|$, irrespective of the value of the principal quantic number ($r = 1$ for $l = 0$; $r = 3$ for $l = 1$ and $m = 0$; $r = 1/2$ for $l = 1$, $|m| = 1$; $r = 11/5$ for $l = 2$, $m = 0$). This derives from the fact that the presence of the functions x, y or z in the quantum integrals affects only the result on the angular part. The same ratio holds for the $\langle p_z^2\rangle/\langle p_x^2\rangle$ term.

Finally, a further exercise can be made on the calculation of the average values of potential and kinetic energies for the hydrogen wavefunctions so as to verify the virial theorem.

In the case of the 1s wavefunction, $\langle V\rangle = \langle 1s|-e^2/r|1s\rangle = -(\pi a_0^3)^{-1}\iiint \exp(-2r/a_0)(e^2/r)r^2 dr \sin\theta d\theta d\varphi =$
$= (-e^2/\pi a_0^3)\int_0^\infty \exp(-2r/a_0) r dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi.$

Since the integral on the radial part is $(a_0/2)^2$, as we have already seen, and the integral on the angular part is 4π, $\langle V\rangle = (-e^2/\pi a_0^3)(a_0/2)^2 4\pi = -e^2/a_0$.
$\langle T\rangle = (\langle p_x^2\rangle + \langle p_y^2\rangle + \langle p_z^2\rangle)/2m = 3\langle p_x^2\rangle/2m = 3\hbar^2/6a_0^2 m = e^2/2a_0$.
Hence it is verified that $\langle T\rangle = -\langle V\rangle/2$.
The extension to the other wavefunctions is straightforward. From the table above, one obtains the value of $\langle T\rangle$ and, considering that $E = -e^2/(2n^2 a_0)$, it is immediate to verify that $E = -\langle T\rangle$, as stated from the virial theorem.

References

[1] This exercise is partly proposed in "Problems and solution in quantum chemistry and physics" by Johnson and Pedersen - Dover Publ., N.Y. (1986) and in "Problems in Quantum Mechanics" by I.I. Gold'man and V.D. Krivchenkov - Dover Publ.- N.Y. (1993).

[2] Handbook of Chemistry and Physics, 76th Edition, CRC Press, p. A-45 (1995).

[3] ibid., p. A-38,39.

The values are in units a_0^2 for $\langle k^2\rangle$, $\hbar^2/a_0^2$ for $\langle p_k^2\rangle$, and $\hbar/2$ for $\Delta k\Delta p_k$ (k=x,y,z).
In all cases, $\langle k\rangle = \langle p_k\rangle = 0$.

	$\langle x^2\rangle=\langle y^2\rangle$	$\langle z^2\rangle$	$\langle p_x^2\rangle=\langle p_y^2\rangle$	$\langle p_z^2\rangle$	$\Delta x\Delta p_x = \Delta y\Delta p_y$	$\Delta z\Delta p_z$
1s	1	1	1/3	1/3	$2/\sqrt{3} \approx 1.15$	$2/\sqrt{3}$
2s	14	14	1/12	1/12	$(14/3)^{1/2} \approx 2.16$	$(14/3)^{1/2}$
$2p_0$	6	18	1/20	3/20	$(6/5)^{1/2} \approx 1.10$	$3(6/5)^{1/2}$
$2p_{\pm1}$	12	6	1/10	1/20	$4(3/10)^{1/2} \approx 2.19$	$(6/5)^{1/2}$
3s	69	69	1/27	1/27	$(2/3)23^{1/2} \approx 3.20$	$(2/3)23^{1/2}$
$3p_0$	36	108	1/45	1/15	$4/\sqrt{5} \approx 1.79$	$12/\sqrt{5}$
$3p_{\pm1}$	72	36	2/45	1/45	$8/\sqrt{5} \approx 3.58$	$4/\sqrt{5}$
$3d_0$	30	66	5/189	11/189	$(10/3)(2/7)^{1/2} \approx 1.78$	$(22/3)(2/7)^{1/2}$