ON THE PRECISION OF QUANTUM MECHANICAL MEAN VALUES COMPUTED BY THE VARIATIONAL METHOD

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Kato[1] and Temple[2] have given a method for estimating the accuracy of approximate eigenvalues for a linear self-adjoint operator. We show that it is also possible to estimate the accuracy of calculated quantum-mechanical mean values of certain functions of the coordinates.

KATO[1] and Temple[2] have given a method for estimating the accuracy with which the variational method yields the eigenvalues of a linear self-adjoint operator. Relying on Kato's results, we give a method of evaluating how accurate is a calculation of the quantum mechanical average of certain functions $F(q)$, where q is the set of coordinates describing the system.

Let H be a linear self-adjoint operator, λ_n its eigenvalues and φ_n its eigenfunctions, which form a complete orthonormal system. Let us assume that the interval (α, β) contains one and only one eigenvalue (λ_p) of the operator H:

$$\begin{aligned}(\lambda_n-\alpha)(\lambda_n-\beta)\geqslant 0, \quad n\neq p;\\ (\lambda_p-\alpha)(\lambda_p-\beta)<0, \quad n=p.\end{aligned} \tag{1}$$

Let ψ_p be an approximation to the function φ_p and expand it in a series of the φ_n: $\psi_p = \Sigma a_n \varphi_n$. If, now, we multiply the first of the inequalities (1) by $|a_n|^2$ and sum over all $n \neq p$ we obtain

$$\sum_{n\neq p}|a_n|^2\lambda_n-(\alpha+\beta)\sum_{n\neq p}|a_n|^2\lambda_n+\alpha\beta\sum_{n\neq p}|a_n|^2\geqslant 0. \tag{2}$$

It is not difficult to see that

$$\overline{H}\equiv(\psi_p, H\psi_p)=\sum_n|a_n|^2\lambda_n, \quad (H\psi_p, H\psi_p)$$
$$=\sum_n|a_n|^2\lambda_n^2, \quad \sum_n|a_n|^2=1,$$

if the trial function ψ_p is normalized. Adding the term with $n = p$ to each sum in (2) and solving for this term, we get

$$\begin{aligned}-|a_p|^2(\lambda_p-\alpha)(\lambda_p-\beta)+\varepsilon^2+(\overline{H}-\alpha)(\overline{H}-\beta)\geqslant 0,\\ \varepsilon^2=(H\psi_p, H\psi_p)-\overline{H}^2.\end{aligned} \tag{3}$$

Identical transformations with the use of the second of the inequalities (1) leads to

$$1-|a_p|^2\leqslant\frac{\varepsilon^2+(\overline{H}-\lambda_p)(\overline{H}+\lambda_p-\alpha-\beta)}{(\lambda_p-\alpha)(\beta-\lambda_p)}\equiv R_p. \tag{4}$$

In order that the interval (α, β) contain the lowest eigenvalue λ_0, it is necessary to take $\alpha = -\infty$, $\beta = \lambda_1$. Then (4) becomes

$$1-|a_0|^2\leqslant(\overline{H}-\lambda_0)/(\lambda_1-\lambda_0). \tag{5}$$

We note that if the interval (α, β) does not contain any eigenvalues of H, then the first of the inequalities (1) holds for all n. Multiplying it by $|a_n|^2$ and summing over all n, we obtain $\epsilon^2 + (\overline{H}-\alpha)(\overline{H}-\beta) \geq 0$. Taking $\alpha = \lambda_0$ and $\overline{H} < \beta < \lambda_1$, we obtain the following lower limit for λ_0:

$$\overline{H}-\varepsilon^2/(\beta-\overline{H})\leqslant\lambda_0. \tag{6}$$

The derivation given above for formulas (4), (5), and (6) has been carried out for a discrete spectrum, but it holds as well when the operator H has a mixed spectrum, with discrete and continuous parts. The inequalities (4) to (6) are derived by a somewhat different method in reference 1.

Given a function $F(q)$, let us evaluate the absolute magnitude of the difference between the true value $\overline{F}_T = (\varphi_p, F\varphi_p)$ of its quantum mechanical average and the approximate value $\overline{F}_A = (\psi_p, F\psi_p)$. The Buniakovski-Schwarz inequality gives

$$\begin{aligned}|\overline{F}_T-\overline{F}_A|=\left|\int F(|\varphi_p|-|\psi_p|)(|\varphi_p|+|\psi_p|)\,dq\right|\\ \leqslant\left[\int|F|^2(|\varphi_p|+|\psi_p|)^2\,dq\cdot\int(|\varphi_p|-|\psi_p|)^2\,dq\right]^{1/2}.\end{aligned} \tag{7}$$

Consider first the integral

$$\int(|\varphi_p|-|\psi_p|)^2\,dq=2\left(1-\int|\varphi_p||\psi_p|\,dq\right).$$

From the inequalities (4), $1-\left|\int\psi_p^*\varphi_p\,dq\right|^2\leq R_p$,

and $\left|\int \psi_p^* \varphi_p \, dq\right| \leq \int |\psi_p|\,|\varphi_p|\, dq$, it immediately follows that

$$\int (|\varphi_p| - |\psi_p|)^2 \, dq \leqslant 2S_p, \quad S_p \equiv 1 - \sqrt{1 - R_p}. \tag{8}$$

We write the second factor in (7) in the form

$$\int |F|^2 (|\varphi_p| + |\psi_p|)^2 \, dq \equiv 4 \int |F|^2 |\psi_p|^2 \, dq$$

$$+ 4 \int |F|^2 |\psi_p| (|\varphi_p| - |\psi_p|) \, dq + \int |F|^2 (|\varphi_p| - |\psi_p|)^2 \, dq.$$

Application of the Buniakovski-Schwarz inequality and inequality (8) then leads to the formula

$$\int |F|^2 (|\varphi_p| + |\psi_p|)^2 \, dq \leqslant 4 \overline{|F|^2}^p + 4 (\overline{|F|^4}^p \cdot 2S_p)^{1/2}$$

$$+ \int |F|^2 (|\varphi_p| - |\psi_p|)^2 \, dq, \tag{9}$$

$$\bar{\varphi}^p = \int \varphi |\psi_p|^2 \, dq.$$

When $|F|$ is bounded, so that $|F|^2 < B$ for all q, we finally obtain

$$|\overline{F}_T - \overline{F}_A| \leqslant \left[2S_p (4 \overline{|F|^2}^p + 4 \sqrt{2S_p \overline{|F|^4}^p} + 2BS_p)\right]^{1/2}. \tag{10}$$

If, on the other hand, $|F|$ increases without limit for sufficiently large q, while $|\varphi_p|^2$ decreases, we can break up the configuration space into two parts I and II, so that $|F|^2 < B$ in the region I and

$$\int\limits_{(II)} |F|^2 (|\varphi_p|^2 + |\psi_p|^2) \, dq \ll \overline{|F|^2}^p$$

because the wave function decreases rapidly. Then

$$\int |F|^2 (|\varphi_p| - |\psi_p|)^2 \, dq \leqslant 2BS_p + \int\limits_{(II)} |F|^2 (|\varphi_p|^2 + |\psi_p|^2) \, dq$$

and we obtain (10) once more.

Similar formulas can be derived for quantum mechanical transition probabilities.

Let φ_n be the real function, ψ an approximation to φ_n. Let us evaluate

$$|(\varphi_m, F\varphi_n) - (\psi_m, F\psi_n)|$$

$$= \left|\int \delta_m F \psi_n \, dq + \int \psi_m F \delta_n \, dq + \int \delta_m F \delta_n \, dq\right|, \tag{11}$$

$$\delta_n = \varphi_n - \psi_n.$$

Assuming that $|F|^2 < B$ for all q, and noting that $\int \delta_n^2 \, dq \leq 2S_n$ ($\int \varphi_n \psi_n \, dq$ is taken to be positive), the Buniakovski-Schwarz inequality gives

$$|(\varphi_m, F\varphi_n) - (\psi_m, F\psi_n)| \leqslant (2S_m \overline{|F|^{2n}})^{1/2}$$

$$+ (2S_n \overline{|F|^{2m}})^{1/2} + 2 (BS_m S_n)^{1/2}. \tag{12}$$

If $|F|$ increases without limit at large q, then we break up the configuration space into two parts, region I where $|F|^2 < B$, and region II in which

$$\int\limits_{(II)} (\psi_m^2 + \varphi_m^2) |F|^2 \, dq \ll \overline{|F|^2}^m,$$

We then obtain (12) once more.

If, in (12), we take $m = n$, we obtain a new inequality for the mean which is sometimes more convenient than the inequality (10).

It is not difficult to see that the right hand sides of (10) and (12) go to zero as the approximation ψ approaches the exact function φ, i.e., for a sufficiently close approximation to φ the estimates here obtained become as accurate as desired.

In applying the above formulas, it is of course not necessary that the approximation ψ be obtained by a straight variational method. It could be obtained by some other approximation procedure (e.g., perturbation theory); the inequalities will then give an estimate of the accuracy of this method. If the energy levels are sufficiently well known, the formulas (10) and (12) can, for example, be used to obtain an estimate of the accuracy of the quantum mechanical calculations of the diamagnetic susceptibility or of transition probabilities in atoms or molecules.

Let us estimate, for example, the accuracy of the calculation of the diamagnetic susceptibility of the helium atom. It is sufficient to consider only the calculation of the mean square radius $\overline{r^2}$. Following Hylleras,[3] we take our approximate ground state wave function to be

$$\psi = Ae^{-sk|2} (1 + 0.08uk + 0.01 t^2 k^2),$$

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|, \quad k = 3.63,$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the radius vectors to the first and second electrons. With this approximation, $\overline{H} = -2.9024$ atomic units; experimentally, the first and second energy levels are $\lambda_0 = -2.9035$ and $\lambda_1 = -2.175$ atomic units.

In applying the inequality (10), we break up the configuration space $\mathbf{r}_1, \mathbf{r}_2$ into region I: $r_1 < 10$ and II: $r_1 > 10$ atomic units. An estimate of the integral $\int |F|^2 (|\varphi_p|^2 + |\psi_p|^2) \, dq$ [neglected in deriving (10)] over the region II shows that this integral is one-millionth of the part retained. Sub-

stituting (5) in (8) and (8) in (10), we obtain $|\overline{F}_T - \overline{F}_A|/|\overline{F}_A| < 0.2$. The diamagnetic susceptibility calculated with the approximation ψ differs from the measured value by less than 1%, which does not disagree with our estimate of the accuracy of the variational method.

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