PHYSICAL REVIEW A VOLUME 45, NUMBER 5 1 MARCH 1992

Matrix elements in the basis of hydrogenic wave functions using an integral transformation

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(Received 16 October 1991)

An integral transformation is given which when applied to hydrogenic-type wave functions converts them into Gaussian form. This is particularly needed in the evaluation of the two-particle matrix elements of the interaction operator. Further examples of the use of the transformation are given by calculating the Wigner transform for the ground state of the H atom and matrix elements of the powers of the z coordinate.

PACS number(s): 31.15.+q

I. INTRODUCTION

In the nonrelativistic quantum mechanics the wave functions of two exactly solvable potentials [1], namely the oscillator potential and the Coulombic potential, are widely used in a very large number of physical problems. The harmonic-oscillator wave functions, because of the Gaussian nature, are easy to separate out into relative and center-of-mass (c.m.) coordinates when one is dealing with the two-particle problem. Since the two-particle potential depends on the relative distance between the two particles, such a transformation is very useful when one is calculating the two-particle matrix elements. This advantage is lost when one is having Coulombic wave functions that are exponential in form. The well-known example is the matrix element of the electron-electron interaction in the ground state of the helium atom. Again because of the Gaussian nature it is trivial to write the Fourier transform of the oscillator wave function, while the same is not true for Coulombic wave functions.

One of the methods that has existed in the literature for quite some time is to either introduce a four-dimensional oscillator [2] or to use the Kustaanheimo-Stiefel transformation and express the coordinates of three-dimensional space in terms of the four dimensions of the oscillator. Because of the extra dimension one has to introduce certain constraints which are used to find the volume element in the four-dimensional space. This volume element is then used in the calculation of the matrix elements of the given operator which is written in terms of the four dimensions of the oscillator.

The object of the present work is to show that an integral transformation can be used to convert the Coulomb wave functions into Gaussian form where such a form is the simplest to use. It will be shown using various examples that the present method provides an extremely simple way to calculate the desired matrix elements.

II. FORMULATION

An integral transformation that has been used quite extensively in the area of many-body physics is the Hubbard-Statanovich transformation, which transforms a Gaussian into an exponential [3]. Here we need a transformation that does the opposite of this. An integral transformation that accomplishes this goal is

$$\int_0^\infty dx\,\exp\left[-x^2-\frac{b^2}{4x^2}\right]=\tfrac{1}{2}\sqrt{\pi}\exp(-b)\,, \tag{1}$$

which has been used in the problem of the generator coordinate wave function [4]. A great advantage of this transformation is that no constrained volume element or further transformation of the operators in terms of new variables is needed. To show explicitly how this transformation simplifies the calculation of matrix elements in the basis of hydrogenic wave functions we shall now consider various examples from one- and two-electron problems. We shall first consider the electron interaction energy in the ground state of He using hydrogenic wave functions [1] $\psi_{100}(\mathbf{r})$ with quantum numbers $n=1$, $l=m=0$. It is given by [1]

$$I=\left[\frac{e^2\alpha^6}{64\pi^2}\right]\int e^{-\alpha(r_1+r_2)}\frac{1}{r_{12}}d\mathbf{r}_1d\mathbf{r}_2\,, \tag{2}$$

where α is written for $2z/a_0$, a_0 being the Bohr radius.

We now apply the integral transformation given by (1) to convert the exponentials into Gaussian. This gives us

$$I=\left[\frac{e^2\alpha^6}{16\pi^3}\right]\int du\,dv\,\exp-(u^2+v^2)\times\int\exp\left[-\left[\frac{\alpha^2}{4u^2}r_1^2+\frac{\alpha^2}{4v^2}r_2^2\right]\right]\times\frac{1}{r_{12}}d\mathbf{r}_1d\mathbf{r}_2\,. \tag{3}$$

The relative $\mathbf{r}$ and c.m. coordinate $\mathbf{R}$ are given by

$$\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2\,, \tag{4a}$$

$$\mathbf{R}=v^2\mathbf{r}_1+u^2\mathbf{r}_2\,. \tag{4b}$$

Using the proper Jacobian, the integral over $\mathbf{r}_1$ and $\mathbf{r}_2$ can be written as

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$$\frac{1}{(u^2+v^2)^3}\int d\mathbf{r}\, d\mathbf{R}\frac{1}{r}\exp\left[-\left[\frac{\alpha^2 r^2}{4(u^2+v^2)}+\frac{\alpha^2 R^2}{4u^2v^2(u^2+v^2)}\right]\right].$$

Carrying out the integration over **r** and **R** and putting it in expression (3), we get

$$I=\left[\frac{4e^2\alpha}{\sqrt{\pi}}\right]\int du\, dv\frac{u^3v^3}{\sqrt{u^2+v^2}}\exp[-(u^2+v^2)]\ . \tag{5}$$

This finally gives us the value for the electron interaction energy I:

$$I=\frac{5e^2\alpha}{16}\ , \tag{6}$$

in agreement with the value given by Schiff [2].

We shall next consider the matrix elements of the powers of z in the basis of hydrogenic wave functions. These are needed in the study of the Stark effect. To bring out the essential points in a simple way, let us consider the matrix element

$$\langle\psi_{1s_0}|z|\psi_{2p_0}\rangle=\frac{\alpha^4}{\sqrt{24\pi}}\int d\mathbf{r}\, r\exp\left[-\frac{3\alpha r}{2}\right]zY_{10}\ , \tag{7}$$

where Y_{10} is the spherical harmonic having $l=1$ and $m=0$. Since $rY_{10}=\sqrt{(3/4\pi)}z$, the matrix element given by (7) using the integral transformation (1) can be rewritten as

$$\langle\psi_{1s_0}|z|\psi_{2p_0}\rangle=\frac{\sqrt{2}\alpha^4}{4\pi^{3/2}}\int dv\exp(-v^2)\times\int d\mathbf{r}\, z^2\exp\left[-\frac{9\alpha^2}{16v^2}r^2\right]. \tag{8}$$

It is obvious that the transformation v has converted the integral into an integral over the oscillator wave functions. Writing $d\mathbf{r}$ as $dx\, dy\, dz$, all the integrals can easily be carried out. This gives us

$$\langle\psi_{1s_0}|z|\psi_{2p_0}\rangle=\frac{256}{243\sqrt{2}\alpha}\ , \tag{9}$$

the same value that one obtains using spherical polar coordinates or using the wave functions of the four-dimensional oscillator [2].

From expression (8) we note the important result that the matrix element of any higher even power of z can be obtained by introducing a parameter in $\exp[-(9\alpha^2/16v^2)r^2]=\exp[-(9\alpha^2/16v^2)(x^2+y^2+z^2)]$ and carrying out differentiation with respect to it.

Our last example will be calculation of Wigner transform $P_W(\mathbf{q},\mathbf{p})$ for the ground state of the H atom. It is defined by [5]

$$P_W(\mathbf{q},\mathbf{p})=(\pi\hbar)^{-3}\int d\mathbf{y}\exp\left[\frac{2i}{\hbar}(\mathbf{p}\cdot\mathbf{y})\right]\times\psi^*_{100}(\mathbf{q}+\mathbf{y})\psi_{100}(\mathbf{q}-\mathbf{y})\ . \tag{10}$$

Using the integral transformation (1) for ψ^*_{100} and ψ_{100} we can write $P_W(\mathbf{q},\mathbf{p})$ as

$$P_W(\mathbf{q},\mathbf{p})=\left[\frac{4\alpha^3}{\pi^2}\right](\pi\hbar)^{-3}\int du\, dv\exp[-(u^2+v^2)]\int d\mathbf{y}\exp\left[\frac{2i}{\hbar}\mathbf{p}\cdot\mathbf{y}\right]\exp\left[-\frac{\alpha^2}{4u^2}|\mathbf{q}+\mathbf{y}|^2\right]\exp\left[-\frac{\alpha^2}{4v^2}|\mathbf{q}-\mathbf{y}|^2\right]. \tag{11}$$

Because of the Gaussians one could now easily integrate over **y** to obtain

$$P_W(\mathbf{q},\mathbf{p})=\left[\frac{32}{\pi^{7/2}\hbar^3}\right]\int du\, dv\exp[-(u^2+v^2)]\frac{(uv)^3}{(u^2+v^2)^{3/2}}\times\exp\left[-\frac{4}{\alpha^2\hbar^2}\frac{u^2v^2}{u^2+v^2}p^2-\frac{2i}{\hbar}\frac{v^2-u^2}{u^2+v^2}\mathbf{p}\cdot\mathbf{q}-\frac{\alpha^2}{u^2+v^2}q^2\right]. \tag{12}$$

Using the transformation

$$u=\rho\cos\theta\ ,\quad v=\rho\sin\theta\ , \tag{13}$$

$P_W(\mathbf{q},\mathbf{p})$ can be written as an integral given by

$$P_W(\mathbf{q},\mathbf{p})=\left[\frac{2}{\pi^{7/2}\hbar^3}\right]\int_0^\infty d\rho\,\rho^4\exp(-\rho^2)\int_0^\pi d\phi\sin^3\phi\exp\left[-\frac{p^2}{\alpha^2\hbar^2}\rho^2\sin^2\phi+\frac{2i}{\hbar}\cos\phi(\mathbf{p}\cdot\mathbf{q})-\frac{\alpha^2}{\rho^2}q^2\right]. \tag{14}$$

As a check on expression (14) of the Wigner transform for the ground state of the H atom, we calculate the distribution of momentum $P(\mathbf{p})$ of the electron in the ground state by integrating over **q**. This gives

$$P(\mathbf{p})=\frac{8}{\pi^2}(\alpha^5\hbar^5)\frac{1}{(p^2+\hbar^2\alpha^2)^4}\ . \tag{15}$$

This is the same expression that one obtains by taking the Fourier transform of $\psi_{100}(\mathbf{r})$ and then writing its absolute square.

III. CONCLUDING REMARKS

We have shown how an integral transformation given by expression (1) can be used to convert hydrogenic wave functions into Gaussian form. The greatest advantage of the present formulation is that no further transformation of the given operator or constraining the volume element is needed. It is particularly useful in the two-particle problem where it allows one to separate the wave function into relative and center-of-mass wave functions thereby eliminating the usual expansion of the two-particle interaction in a series of Legendre polynomials.

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