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THEOREMS SATISFIED BY VARIATIONAL WAVE FUNCTIONS IN SCATTERING THEORY \*

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## I. INTRODUCTION

This report is a revision of the second part of an earlier report.<sup>1</sup> Our interest in the subject was reawakened by reading the paper of Heaton and Moiseiwitsch<sup>2</sup> which, among other things, led us to the realization that many of our earlier results were derived under unnecessarily severe restrictions.<sup>3</sup>

Our goal is to derive various theorems in the theory of scattering of a spin-less particle by a real central potential, directly from the Kohn variation principle.<sup>4</sup> Such an approach provides a unified view of the theorems and also, as a by product, yields sufficient conditions under which an optimal variational wavefunction will satisfy analogous theorems.<sup>5</sup>

II. THE KOHN VARIATION PRINCIPLE<sup>4</sup>

Some Definitions:

$$(A, B) \equiv \int_0^{\infty} dr A^* B \quad (1)$$

$$H_l = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2m r^2} + V(r) = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + U(r) \quad (2)$$

$$E = \frac{\hbar^2 k^2}{2m} \quad (3)$$

Let  $\psi_l$  be a trial function satisfying the asymptotic condition<sup>6</sup>

$$\psi_l \xrightarrow{R \rightarrow \infty} \psi_l^{\infty} \equiv \frac{1}{k} \sin \left( kr - \frac{l\pi}{2} \right) + \lambda_l \cos \left( kr - \frac{l\pi}{2} \right) \quad (4)$$

where  $\lambda_e$  is independent of  $R$ . Then the Kohn variation principle states that

$$\delta [\lambda_e] = 0 \quad (5)$$

where

$$[\lambda_e] \equiv \lambda_e + 2m (\psi_e, (E - H_e) \psi_e) \quad (6)$$

and where, from (4) the variations of  $\psi_e$  satisfy the asymptotic condition

$$\delta \psi_e \xrightarrow{R \rightarrow \infty} \delta \lambda_e \cos(kR - \frac{e\pi}{2}) \quad (7)$$

In a moment we will derive the Kohn variation principle. That is we will show that if the  $\delta \psi_e$  are otherwise unrestricted then (5) implies and is implied by the Schrödinger equation

$$(E - H_e) \psi_e = 0 \quad (8)$$

Therefore since, when (8) is satisfied, we have  $[\lambda_e] = \lambda_e$ , we see that  $[\lambda_e]$  provide a variational approximation to the true  $\lambda_e$  ( $k \lambda_e = \tan \delta_e$  where  $\delta_e$  is the phase shift).

Written out more explicitly (5) is evidently

$$0 = \delta \lambda_e + 2m (\delta \psi_e, (E - H_e) \psi_e) + 2m (\psi_e, (E - H_e) \delta \psi_e) \quad (9)$$

Further by an integration by parts, and by use of (1) and (6) it is easy to show that<sup>7</sup>

$$0 \equiv \delta \lambda_e + 2m (H_e \psi_e, \delta \psi_e) - 2m (\psi_e, H_e \delta \psi_e)$$

Thus we may write (9) in the same form as the familiar bound state variation principle, namely<sup>8</sup>

$$0 = (\delta \psi_e, (E - H_e) \psi_e) + ((E - H_e) \psi_e, \delta \psi_e) \quad (10)$$

in which form it is clear that with  $\delta \psi_e$  arbitrary, the Kohn variation principle implies and is implied by the Schrödinger equation.

Finally we make a simplification - clearly there is no need to introduce complex wave functions, so we won't do so. <sup>Then</sup> Since with  $\psi_e$  real the two terms in (10) are equal to one another, we can replace (9) and (10) by

$$0 = \delta \lambda_e + 2m (\psi_e, (E - H_e) \delta \psi_e) \quad (11)$$

and

$$0 = (\delta \psi_e, (E - H_e) \psi_e) \quad (12)$$

These, together with (6), the asymptotic conditions (4) and (7), and the definitions (1) - (3) are then our basic equations.

### III. THE GENERALIZED HELLMANN-FEYNMAN THEOREM

Let  $\mu$  be a real parameter in  $\mathbb{V}$ . Then differentiating (6) with respect to  $\mu$  we find

$$\begin{aligned} \frac{\partial \langle \lambda_2 \rangle}{\partial \mu} &= -2m \left( \psi_2, \frac{\partial V}{\partial \mu} \psi_2 \right) + \\ &+ \frac{\partial \lambda_2}{\partial \mu} + 2m \left( \frac{\partial \psi_2}{\partial \mu}, (E - H_0) \psi_2 \right) + 2m \left( \psi_2, (E - H_0) \frac{\partial \psi_2}{\partial \mu} \right) \end{aligned} \quad (13)$$

We now note that

$$\delta \psi_2 = \frac{\partial \psi_2}{\partial \mu} \delta \mu \quad (14)$$

satisfies (7) with

$$\delta \lambda = \frac{\partial \lambda}{\partial \mu} \delta \mu \quad (15)$$

whence we see from (11) and (12) that the sum of the last three terms in (13) vanishes so that

$$\frac{\partial \langle \lambda_2 \rangle}{\partial \mu} = -2m \left( \psi_2, \frac{\partial V}{\partial \mu} \psi_2 \right) \quad (16)$$

which by analogy with the bound state case, we call the generalized Hellmann-Feynman theorem. For exact wave functions it is a well known result.<sup>9</sup> In a variation calculation (14) will be a possible variation of  $\psi_2$ , and hence (16) will be satisfied by the optimal trial function, provided that the set of trial functions is independent of  $\mu$ .<sup>10</sup>

#### IV. INTEGRAL HELLMANN-FEYNMAN THEOREM

Let  $\overline{\psi}_2$  be an optimal trial function for a potential  $\overline{V}$ .

Then since

$$\bar{\Psi}_e^\infty = \frac{1}{k} \sin(kR - \frac{2\pi}{\lambda}) + \bar{\gamma}_e \cos(kR - \frac{2\pi}{\lambda})$$

we see that if  $\delta E$  is a real constant then

$$(\bar{\Psi}_e^\infty - \Psi_e^\infty) \delta E = (\bar{\gamma}_e - \gamma_e) \delta E \cos(kR - \frac{2\pi}{\lambda})$$

is of the form (7) with

$$\delta \gamma_e = (\bar{\gamma}_e - \gamma_e) \delta E \quad (17)$$

Thus we can choose

$$\delta \Psi_e = (\bar{\Psi}_e - \Psi_e) \delta E \quad (18)$$

whence we find from (11), using (17) and (6) that

$$0 = \bar{\gamma}_e - [\gamma_e] + 2m (\Psi_e, (E - H_e) \bar{\Psi}_e)$$

or

$$0 = \bar{\gamma}_e + 2m (\Psi_e, (E - \bar{H}_e) \bar{\Psi}_e) - [\gamma_e] + 2m (\Psi_e, (\bar{H}_e - H_e) \bar{\Psi}_e) \quad (19)$$

We now note that if we choose, as we may

$$\delta \bar{\Psi}_e = (\Psi_e - \bar{\Psi}_e) \delta E \quad (20)$$

then we find from (12) [i.e., (12) with  $\bar{\Psi}_e$  everywhere]

$$0 = (\Psi_e, (E - \bar{H}_e) \bar{\Psi}_e) - (\bar{\Psi}_e, (E - \bar{H}_e) \bar{\Psi}_e) \quad (21)$$

Thus we can write (19) as

$$0 = \bar{\lambda}_e + 2m (\bar{\psi}_e, (\bar{E} - \bar{H}_e) \bar{\psi}_e) - [\bar{\lambda}_e] + 2m (\psi_e, (\bar{H}_e - H_e) \bar{\psi}_e)$$

whence from (6) we have finally

$$0 = [\bar{\lambda}_e] - [\bar{\lambda}_e] + 2m (\psi_e, (\bar{H}_e - H_e) \bar{\psi}_e) \quad (22)$$

which, for exact wave functions, is a well-known result.<sup>11</sup> Also it is clearly the continuum analogue of the so-called integral Hellmann-Feynman Theorem for bound states.<sup>12</sup>

In a variation calculation (18) and (20) will be possible variations of  $\psi_e$  and  $\bar{\psi}_e$  respectively, and hence (22) will be satisfied by the optimal trial functions provided that  $\psi_e = \chi$  and  $\bar{\psi}_e = \chi$  where  $\chi$  is any given function such that

$$\chi \xrightarrow{R \rightarrow \infty} \frac{1}{k} \sin(kR - \frac{e\pi}{2})$$

are chosen from a common linear space of trial functions.<sup>13</sup>

## V. A SIMILAR THEOREM

The theorem of the preceding section describes what happens if we change  $V$  at fixed  $l$ . Now we investigate the effects of changing  $l$  at fixed  $V$ . First let  $l' > l$  be of the form

$$l' = l + 4m$$

where  $m$  is an integer. Then we can write

$$\psi_{l'}^{\infty} = \frac{1}{k} \sin(kR - \frac{e\pi}{2}) + \gamma_{l'} \cos(kR - \frac{e\pi}{2})$$

and

$$\psi_l^{\infty} = \frac{1}{k} \sin(kR - \frac{e'\pi}{2}) + \gamma_l \cos(kR - \frac{e'\pi}{2}) \quad (23)$$



whence

$$\delta\psi_e = (\psi_{e'} - \psi_e) \delta\epsilon \quad (24)$$

satisfies (7) with

$$\delta\lambda_e = (\lambda_{e'} - \lambda_e) \delta\epsilon \quad (25)$$

From (11) and (6) we then find, after some rearranging

$$0 = \lambda_{e'} + (\psi_e, (E - H_{e'}) \psi_{e'}) - [\lambda_e] + 2m (\psi_e, (H_{e'} - H_e) \psi_{e'}) \quad (26)$$

Further from (23) we see that we may choose

$$\delta\psi_{e'} = (\psi_e - \psi_{e'}) \delta\epsilon \quad (27)$$

which, when inserted into (12)' yields

$$0 = (\psi_e, (E - H_{e'}) \psi_{e'}) - (\psi_{e'}, (E - H_{e'}) \psi_{e'}) \quad (28)$$

Thus we can write (26) as

$$0 = [\lambda_{e'}] - [\lambda_e] + 2m (\psi_e, (H_{e'} - H_e) \psi_{e'}); \quad e' = e + 4m \quad (29)$$

which is a known theorem.<sup>14</sup>

For even wave functions

For the case  $e' = e + 4m + 2$

we proceed in a similar

fashion except that now we can write

$$\begin{aligned} \psi_{e'}^{\infty} &= -\frac{1}{k} \sin(kx - e'\pi) - \lambda_{e'} \cos(kx - e'\pi) \\ \psi_e^{\infty} &= -\frac{1}{k} \sin(kx - e\pi) - \lambda_e \cos(kx - e\pi) \end{aligned} \quad (30)$$

whence we can choose

$$\delta\psi_e = (\psi_e + \psi_{e'}) \delta\epsilon \quad (31)$$

with

$$\delta\lambda_e = (\lambda_e - \lambda_{e'}) \delta\epsilon \quad (32)$$

and also we can use

$$\delta\psi_{e'} = (\psi_e + \psi_{e'}) \delta\epsilon \quad (33)$$

The result is then

$$0 = [\lambda_e] - [\lambda_{e'}] + 2m (\psi_e, (H_{e'} - H_e) \psi_{e'}) ; l' = l + 4m + 2 \quad (34)$$

which ~~is~~ again for exact wave functions is a known result.<sup>14</sup>

In a variation calculation (24) and (27) will be possible variations of  $\psi_e$  and  $\psi_{e'}$  and therefore (29) will be satisfied if  $\psi_e - \chi$  and  $\psi_{e'} - \chi$ , with  $\chi$  defined as in the previous section, are chosen from a common linear space of trial functions. Similarly one will have (34) if  $\psi_e - \chi$  and  $\psi_{e'} + \chi$  are chosen from a common linear space.

Next we consider the ~~case~~

$$l' = l + 4m + 1$$

Here we can write

$$\psi_{e'}^{(0)} = -\frac{1}{k} \cos(kr - \frac{2\pi}{2}) + \lambda_{e'} \sin(kr - \frac{2\pi}{2}) \quad (35)$$

and

$$\psi_0^{\infty} = \frac{1}{k} \cos(kR - \frac{e'\pi}{2}) - \lambda_2 \sin(kR - \frac{e'\pi}{2}) \quad (36)$$

Then we see that

$$\delta\psi_2 = \left( \psi_2 - \frac{1}{k\lambda_2'} \right) \delta E \quad (37)$$

satisfies (7) with

$$\delta\lambda_2 = \left( \lambda_2 + \frac{1}{k^2 \lambda_2'} \right) \delta E \quad (38)$$

and also we see that

$$\delta\psi_2' = \left( \psi_2' + \frac{1}{k\lambda_2} \right) \delta E \quad (39)$$

satisfies (7)'. Proceeding in the standard way one then finds rather messy result: <sup>the</sup> that  $\rho \sim$

$$d' = d + 4m + 2$$

$$0 = k\lambda_2' [\lambda_2] - k\lambda_2' \lambda_2 + k [\lambda_2'] \lambda_2 + \frac{1}{k} - 2m(\psi_2', (H_2' - H_2)\psi_2) \quad (40)$$

which, in case the Schrödinger equation is satisfied on average<sup>3</sup> i.e., so that  $(\psi_2, (E - H_2)\psi_2) = (\psi_2', (E - H_2)\psi_2')$  whence

$$[\lambda_2] = \lambda_2, \quad [\lambda_2'] = \lambda_2'$$

reduces to the form of the known result for exact functions.<sup>14</sup> However of itself (40) does not seem especially interesting. Also it is not at

all clear to us how to ensure that (37) and (39) are possible variations so we will not pursue the matter further. The case  $l' = l + 4n + 3$  yields similar results. In Section VIII we will derive rather nicer theorems for these cases.

## VI. THE VIRIAL THEOREM

We now observe, essentially following Robinson and Hirschfelder<sup>15</sup>, that

$$W \psi_e^\infty \equiv \left( R \frac{d}{dR} - k \frac{d}{dk} - 1 \right) \psi_e^\infty = -\frac{d}{dk} (k \lambda_e) \cos(kR - \frac{l\pi}{2}) \quad (41)$$

Thus

$$\delta \psi_e = \delta E W \psi_e \quad (42)$$

satisfies (7) with

$$\delta \lambda_e = -\frac{d}{dk} (k \lambda_e) \delta E \quad (43)$$

Inserting these results in (11) and (12) we therefore have

$$0 = -\frac{d}{dk} (k \lambda_e) + 2m \langle \psi_e, (E - H_e) W \psi_e \rangle \quad (44)$$

and

$$0 = \langle W \psi_e, (E - H_e) \psi_e \rangle \quad (45)$$

Since  $(E - H_e) \psi_e$  vanishes asymptotically one may freely integrate by parts in (45) in order to transfer the  $d/dR$  to the right.

Also one may ~~transfer~~ transfer the  $d/dk$  to the right by noting that differentiations of (6) yields

$$\frac{d[E\psi_e]}{dk} = \frac{d\lambda_e}{dk} + 2m \left( \frac{\partial \psi_e}{\partial k}, (E - H_e) \psi_e \right) + 2m \left( \psi_e, \frac{\partial}{\partial k} (E - H_e) \psi_e \right) \quad (46)$$

Then using these results one finds, after a bit of rearranging, that (45) can be written as

$$0 = (\psi_e, W(E - H_e) \psi_e) + \frac{1}{2m} k \frac{d[E\psi_e]}{dk} - \frac{1}{2m} k \frac{d\lambda_e}{dk} - 3(\psi_e, (E - H_e) \psi_e) \quad (47)$$

Subtracting this from (44) then yields

$$0 = -\frac{d}{dk} k[E\psi_e] + 2m (\psi_e, [(E - H_e), W] \psi_e) - 2(\psi_e, (E - H_e) \psi_e) \quad (48)$$

which becomes, on evaluating the commutator,

$$0 = -\frac{d}{dk} k[E\psi_e] + 2m (\psi_e, (2V + R \frac{dV}{dR}) \psi_e) \quad (49)$$

which for exact wave functions is the virial theorem<sup>16</sup> (Note that in (49)  $V$  can also be replaced by  $U$ ).

In a variation calculation one can ensure that (42) is a possible variation of  $\psi_e$  by introducing a variation (scaling) parameter as follows: Let  $\frac{1}{k} \phi(k, R)$  satisfy the asymptotic conditions. Then one readily sees that

$$\psi_e = \frac{1}{k} \phi\left(\frac{k}{2}, 2R\right) \quad (50)$$

will also satisfy the conditions, and further one sees that

$$\delta E W \psi_e = \frac{\delta \psi_e}{\delta E} \delta E \quad (51)$$

where  $E = \ln \eta$ , as desired. The trial functions used in the first of references 2 are (aside from a difference in notation<sup>6</sup>) precisely of the class (50). More generally if  $K$  times the set of trial functions is invariant to  $R \rightarrow \eta R$ ,  $K \rightarrow \frac{K}{\eta}$  then (49) will be satisfied.

#### VII. HYPERVIRIAL THEOREMS

See the second of References 1.

#### VIII. GENERALIZED TIETZ' THEOREMS

Returning to the case

$$l' = l + 4m + 1$$

which we considered in Sec. V we now note from (35) that we can make a rather simple connection between  $\psi_{e'}^{\infty}$  and  $\psi_e^{\infty}$ , namely

$$\frac{1}{k} \frac{d\psi_{e'}^{\infty}}{dR} = \frac{1}{k} \sin(kR - \frac{2l'\pi}{2}) + \lambda_{e'} \cos(kR - \frac{2l'\pi}{2}) \quad (52)$$

so that

$$\delta \psi_e = \left( \frac{1}{k} \frac{d\psi_{e'}}{dR} - \psi_e \right) \delta E \quad (53)$$

satisfies (7) with

$$\delta \lambda_e = (\lambda_{e'} - \lambda_e) \delta E \quad (54)$$

Thus we find from (11) that

$$0 = \lambda_{e'} - [\lambda_e] + \frac{2m}{k} (\psi_{e'}, (E - H_e) \frac{d\psi_{e'}}{dr}) \quad (55)$$

However from (36) we also have

$$\frac{1}{k} \frac{d^2 \psi_{e'}}{dr^2} = -\frac{1}{k} \sin(kR - r' \pi_e) - \lambda_e \cos(kR - r' \pi_e) \quad (56)$$

so

$$\delta \psi_{e'} = (\psi_{e'} + \frac{1}{k} \frac{d\psi_{e'}}{dr}) \delta E \quad (57)$$

satisfies (7)', whence (12)' yields

$$0 = (\psi_{e'}, (E - H_{e'}) \psi_{e'}) + (\frac{1}{k} \frac{d\psi_{e'}}{dr}, (E - H_{e'}) \psi_{e'}) \quad (58)$$

or, integrating by parts

$$0 = (\psi_{e'}, (E - H_{e'}) \psi_{e'}) - \frac{1}{k} (\psi_{e'}, \frac{d}{dr} (E - H_{e'}) \psi_{e'}) \quad (59)$$

Multiplying this by  $2m$  and adding to (55) then yields the result

$$0 = [\lambda_{e'}] - [\lambda_e] + \frac{2m}{k} (\psi_{e'}, (\frac{d}{dr} H_{e'} - H_e \frac{d}{dr}) \psi_{e'}) \quad (60)$$

Unhappily it is not clear to us how one could arrange for (60) to be satisfied in a variation calculation, i.e., for (53) and (57) to be possible variations.

Equation (60) is, for exact wave functions, in fact essentially the same as results given already by Tietz<sup>17</sup> (in the case  $l' = l + 1$ ) and more generally by Fradkin and Calogero.<sup>18</sup> To see this one first notes that in carrying out the operations in the integrand of (60) one encounters derivatives of  $\psi_{l'}$ . However these can be eliminated as follows: Evidently

$$\delta\psi_{l'} = r^{-1} \psi_{l'} \quad \text{and} \quad \delta\psi_l = r^{-1} \psi_l \quad (61)$$

satisfy (7) and (7') respectively with

$$\delta\lambda_{l'} = \delta\lambda_l = 0 \quad (62)$$

From (11) and (12') then we find

$$0 = (\psi_{l'}, (E - H_{l'}) \frac{1}{r} \psi_{l'}) \quad (63)$$

$$0 = (\frac{1}{r} \psi_l, (E - H_l) \psi_{l'}) \quad (64)$$

which by subtraction yields

$$0 = (\psi_{l'}, (\frac{1}{r} H_{l'} - H_l \frac{1}{r}) \psi_{l'}) \quad (65)$$

Carrying out the operations in the integrands of (60) and (65) and combining them yields

$$0 = [\lambda_{l'}] - [\lambda_l] + 2m(\psi_{l'}, \left[ \frac{dV}{dr} + \frac{[(l'-l)^2 - 1](l+l'+2)(l+l')}{2r^3} \right] \frac{1}{r} \psi_{l'}) \quad (66)$$



which, for exact wave functions, is the result given by Fradkin and Calogero.<sup>18</sup> The case

$$l' = l + 4m + 3$$

can be discussed in a similar way and yields the result given in Reference 18 but with  $[\lambda]'$ 's instead of  $\lambda$ 's again. For  $l' = l + 4m$  and  $l' = l + 4m + 2$ , the straightforward results are more complicated (involving both  $\lambda$ 's and  $[\lambda]'$ 's as in (40)) and presumably even less interesting (to repeat, we really don't know how, in a practical way, to guarantee any of the results of this section variationally) so we will not go into details.

## FOOTNOTES AND REFERENCES

1. WIS-TCI-216, January 1967. This report in turn was an extension of S. T. Epstein and P. D. Robinson, Phys. Rev. 129, 1396 (1963).
2. M. Heaton and B. L. Moiseiwitsch, J. Phys. B 4, 322 (1971). See also J. D. G. McWhirter and B. L. Moiseiwitsch, J. Phys. B 5, 1439 (1972).
3. Namely that, in the notation we will be using,  $(\psi_e, (E-H_e)\psi_e) = 0$ ,  $(\psi_e', (E-H_e')\psi_e') = 0$ , etc. - something which is rarely true in variational calculations based on the Kohn variation principle.
4. W. Kohn, Phys. Rev. 74, 1763 (1948).
5. No doubt also our methods can be extended to other situations - theorems satisfied by the full scattering amplitude (we will deal only with individual partial waves), electron-atom collisions etc. See Epstein and Robinson, Reference 1; also Reference 2; and also M. B. McElroy and J. O. Hirschfelder, Phys. Rev. 131, 1589 (1963).
6. In the References 2 a slightly different notation is used. Their  $u$  is  $K$  times our  $\psi_e$ , their  $\lambda_T$  is  $K$  times our  $\lambda_e$  and their  $\lambda_V$  is  $K$  times our  $[\lambda_e]$ .
7. To derive (9) one also needs

$$\left( \psi_e \frac{d(\delta\psi_e)}{dr} - \delta\psi_e \frac{d\psi_e}{dr} \right)_{r=0} = 0$$

We will assume that this is true without further comment.

8. This form is of interest in connection with the work of K. R. Brownstein, and W. A. McKinley, Phys. Rev. 170, 1255 (1968). See also H. J. Kolker, J. Chem. Phys. 53, 4697 (1970).

9. W. A. McKinley and J. H. Macek, Phys. Lett. 10, 210 (1964); and R. Sugar and R. Blankenbecler, Phys. Rev. 136, B472 (1964). See also W. E. Smith, N. Cim. 39, 216 (1965).
10. A. C. Hurley, Proc. Roy. Soc. A226, 1179 (1959).
11. See for example A. Messiah, "Quantum Mechanics" Vol. I (North Holland Publ. Co., Amsterdam, 1961) page 404.
12. R. G. Parr, J. Chem. Phys. 40, 3726 (1964).
13. S. T. Epstein, A. C. Hurley, R. E. Wyatt, R. G. Parr, J. Chem. Phys. 47, 1275 (1967).
14. See for example D. M. Fradkin and F. Calogero, Nuc. Phys. 75, 475 (1966) Equation (14). Note that their  $y_e$  is  $\kappa \cos \delta_e$  times our  $\psi_e$ .
15. P. D. Robinson and J. O. Hirschfelder, Phys. Rev. 129, 1391 (1963).
16. Y. N. Demkov, Doklady Akad. Nauk. (USSR) 138, 86 (1961).
17. T. Tietz, Nuclear Physics 44, 633 (1963). This theorem is also equivalent to Gerjuoy's momentum transfer cross-section theorem (see E. Gerjuoy, J. Math. Phys. 6, 993 (1965), especially Equation (23)).
18. Reference 14, Eqn. (15).