Constants of Motion for Separable One-Particle Problems with Cylinder Symmetry*

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For those cylindrically symmetrical one-particle problems which are separable in either prolate spheroidal or parabolic coordinates, a quantum mechanical constant of the motion and its classical analogue are independently derived and compared. The quantum mechanical constant of the motion is a sum of an operator depending only on the coordinate system chosen and possessing a simple physical significance and of a second operator uniquely linked with the special separable potential chosen. The superposition principle for separable potentials also holds for the corresponding operators mentioned before. This constant of the motion does not result from spatial symmetry but from separability. It also must, however, be taken into account for the classification of energy levels depending on a parameter to avoid violations of the non-crossing rule. The formal theory given is applied to several special problems.

Für diejenigen zylindersymmetrischen Einteilchen-Probleme, die sich in elliptischen oder parabolischen Koordinaten separieren lassen, werden eine quantenmechanische Erhaltungsgröße und ihr klassisches Analogon unabhängig voneinander abgeleitet und verglichen. Die quantenmechanische Erhaltungsgröße ist jeweils die Summe eines Operators, der nur vom gewählten Koordinatensystem abhängt und eine einfache physikalische Bedeutung besitzt, und eines zweiten Operators, der eindeutig mit dem gewählten separierbaren Potential verknüpft ist. Das Superpositionsprinzip für separierbare Potentiale überträgt sich auf die zugehörigen, eben genannten Operatoren. Diese Erhaltungsgröße folgt nicht aus der räumlichen Symmetrie. Sie muß jedoch bei der Klassifikation von Energietermen, die von einem Parameter abhängen, mitberücksichtigt werden, um scheinbare Verletzungen der Nichtkreuzungsregel zu vermeiden. Die formale Theorie wird auf mehrere spezielle Probleme angewandt.

Introduction

The problem of classifying the electronic states of atomic and molecular systems with several electrons and of finding the terms resulting from a given electronic configuration has been solved by several authors. The most elegant, group theoretical solution of the latter problem for molecules was certainly given by Hansen [1, 2]. All solutions of this problem are essentially based on the concept of the spatial symmetry group, the largest subgroup of the full rotation-reflection group O_3 consisting of operations which leave the Hamiltonian invariant, and on the properties of its irreducible representations.

This concept of spatial symmetry, however, fails to be efficient for some one-electron problems. "Accidental" degeneracies of energy terms occur for the two- and three-dimensional isotropic harmonic oscillator and for the hydrogen atom; energy levels belonging to different irreducible representations of the spatial

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* Dedicated to the memory of Professor K. H. Hansen.

symmetry group coincide[1]. In the H_2^+-problem, the energy terms $2s\sigma_g$ and $3d\sigma_g$, belonging to the same irreducible representation σ_g^+ of the *spatial* symmetry group $D_{\infty h}$ do cross in spite of the non-crossing rule. When an expression like $Q/(r_1 \cdot r_2)$ (which preserves separability) is added to the two-centre Coulomb potential $Z_1/r_1 + Z_2/r_2$, the energy levels $2s\sigma_g$ and $3d\sigma_g$ still cross [3]. This last example of degeneracy induced us to study separability, a common feature of all problems mentioned above, in order to try to relate it to a higher symmetry not included in spatial symmetry. Of greatest importance for our aim there proved to be those coordinate systems in which the solutions of the Schrödinger equation separate completely in the spatial variables, but only partially in the separation constants (class *B* of Morse's classification [5, p. 518]). The most important coordinate systems of this class are the (rotational) prolate spheroidal and the (rotational) parabolic systems.

Cylindrically Symmetrical Potentials Separable in Prolate Spheroidal Coordinates

1. Prolate spheroidal coordinates μ, v, φ are as usually defined by

$$\mu = \frac{r_1 + r_2}{R} \quad v = \frac{r_1 - r_2}{R} \quad \varphi \tag{1}$$

and are related to cylinder coordinates ϱ, φ, z by

$$\varrho = \sigma \sqrt{(\mu^2 - 1)(1 - v^2)} \quad z = \sigma \mu v \quad \varphi = \varphi . \tag{2}$$

The most general cylindrically symmetrical potential energy V for which the Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2M} \Delta + V \right\} \chi = \varepsilon \chi \tag{3}$$

separates in prolate spheroidal coordinates is of the form

$$V(\mu, v) = \frac{V_1(\mu) + V_2(v)}{\mu^2 - v^2} \tag{4}$$

according to Eisenhart [4] or Morse and Feshbach [5, p. 661]. Let us first construct a classical constant of the motion and then return to quantum mechanics.

An easy calculation shows:

Canonical momenta p_μ, p_v, p_φ which are conjugated to the variables μ, v, φ are

$$p_\mu = M\sigma^2 \frac{\mu^2 - v^2}{\mu^2 - 1} \dot{\mu}$$

$$p_v = M\sigma^2 \frac{\mu^2 - v^2}{1 - v^2} \dot{v} \tag{5}$$

$$p_\varphi = M\sigma^2 (\mu^2 - 1)(1 - v^2) \dot{\varphi} .$$

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[1] H. V. McIntosh gives an excellent survey in his paper "Symmetry and degeneracy" contained in the second volume of "Group theory and its applications", ed. E. M. Loebl, New York: Acad. Press 1971.
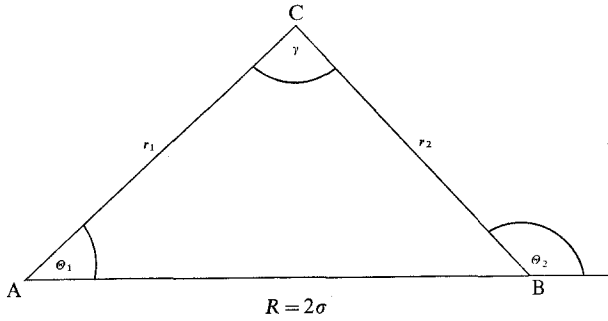
Fig. 1

The Hamiltonian function for a particle with mass M and potential energy V is

$$H(\mu, v, \varphi; p_\mu, p_v, p_\varphi)$$

$$= \frac{1}{2M\sigma^2(\mu^2 - v^2)} \left\{ (\mu^2 - 1) p_\mu^2 + (1 - v^2) p_v^2 + \left(\frac{1}{\mu^2 - 1} + \frac{1}{1 - v^2} \right) p_\varphi^2 \right\} + V \tag{6}$$

(see, for instance [6, p. 178]).

As the Schrödinger equation with V given according to Eq. (4) separates, so does the Hamilton-Jacobi Eq. [4a]:

$$H\left(\mu, v, \varphi; \frac{\partial S_0}{\partial \mu}, \frac{\partial S_0}{\partial v}, \frac{\partial S_0}{\partial \varphi} \right) = E \tag{7}$$

for the characteristic function $S_0(\mu, v, \varphi) = S + E \cdot t$. With the ansatz

$$S_0(\mu, v, \varphi) = p_\varphi \cdot \varphi + S_1(\mu) + S_2(v), \tag{8}$$

where p_φ is a first constant of the motion, we obtain from (7):

$$(\mu^2 - 1) \left(\frac{dS_1}{d\mu} \right)^2 + \frac{p_\varphi^2}{\mu^2 - 1} + 2M\sigma^2 (V_1(\mu) - E(\mu^2 - 1)) = \beta \tag{9a}$$

$$(1 - v^2) \left(\frac{dS_2}{dv} \right)^2 + \frac{p_\varphi^2}{1 - v^2} + 2M\sigma^2 (V_2(v) - E(1 - v^2)) = -\beta. \tag{9b}$$

Note that β is not uniquely defined by (4) and (7). Eqs. (9a) and (9b) may be multiplied with a common factor independent of μ, v, φ, and if a constant independent of μ, v, φ (but perhaps depending on E and p_φ) is added to β, it cancels when (9a) and (9b) are added to give Eq. (5). In fact, (9a) and (9b) realize a convention frequently used.

We now replace $\partial S_0/\partial \mu = dS_1/d\mu$ by p_μ and $\partial S_0/\partial v = dS_2/dv$ by p_v in (9a) and (9b) respectively, then multiply (9a) with $1 - v^2$ and (9b) with $-(\mu^2 - 1)$. Adding and thus eliminating E, we finally obtain

$$\beta = \frac{(\mu^2 - 1)(1 - v^2)}{\mu^2 - v^2} (p_\mu^2 - p_v^2) + \left(\frac{1}{\mu^2 - 1} - \frac{1}{1 - v^2} \right) p_\varphi^2$$

$$+ 2M\sigma^2 \frac{(1 - v^2) V_1(\mu) - (\mu^2 - 1) V_2(v)}{\mu^2 - v^2}. \tag{10}$$

The first two terms of this expression (first line) are independent of the special potential chosen.

Using the relations

$$L^2 = \frac{\mu^2 + v^2 - 1}{(\mu^2 - 1)(1 - v^2)} p_\mu^2 + \frac{(\mu^2 - 1)(1 - v^2)}{(\mu^2 - v^2)^2} (\mu p_\mu - v p_v)^2, \qquad (11)$$

$$p_\varrho = M\dot\varrho = \frac{(\mu^2 - 1)(1 - v^2)}{\sigma(\mu^2 - v^2)} (\mu p_\mu - v p_v) \qquad (12)$$

for the square of angular momentum $\vec{L} = \vec{r} \times \vec{p}$ and the momentum p_ϱ conjugate to $\varrho = \sqrt{x^2 + y^2}$, we finally obtain[2]

$$\beta = -L^2 + \sigma^2 \left(p_\varrho^2 + \frac{p_\varphi^2}{\varrho^2} \right) + 2M\sigma^2 \frac{(1 - v^2) V_1(\mu) - (\mu^2 - 1) V_2(v)}{\mu^2 - v^2}$$

$$= -L^2 + \sigma^2(p_x^2 + p_y^2) + \beta_{\text{pot}}. \qquad (13)$$

The linear combination of two separable potential energies V, V' is again a separable potential V'', so the domain of separable potentials is a function space. As the potential part β_{pot} of β is linear in V_1 and V_2, the process of constructing $\beta_{\text{pot}} = \tilde{V}$ from V is a linear mapping of a function space $\{V\}$ on a second function space $\{\beta_{\text{pot}}\}$:

$$\widetilde{cV} = c\tilde{V}$$
$$\widetilde{V + V'} = \tilde{V} + \tilde{V}' \qquad (c \in \mathbb{R}). \qquad (14)$$

2. Let us now return to quantum mechanics. The Schrödinger Eq. (4) separates with the ansatz

$$\chi(\mu, v, \varphi) = F(\mu)\, G(v)\, e^{\mathrm{i} m \varphi} \qquad (15)$$

and gives

$$\left\{ \hbar^2 \left(-\frac{\partial}{\partial \mu} (\mu^2 - 1) \frac{\partial}{\partial \mu} + \frac{m^2}{\mu^2 - 1} \right) + 2M\sigma^2(V_1(\mu) - \varepsilon(\mu^2 - 1)) - A' \right\} F(\mu) \quad (16\text{a})$$
$$= 0$$

$$\left\{ \hbar^2 \left(-\frac{\partial}{\partial v} (1 - v^2) \frac{\partial}{\partial v} + \frac{m^2}{1 - v^2} \right) + 2M\sigma^2(V_2(v) - \varepsilon(1 - v^2)) + A' \right\} G(v) \quad (16\text{b})$$
$$= 0.$$

Note the similarity of (16) with (9).

Now (16a) is multiplied with $(1 - v^2)\, G(v)\, e^{\mathrm{i} m \varphi}$ and (16b) is multiplied with $-(\mu^2 - 1)\, F(\mu)\, e^{\mathrm{i} m \varphi}$. We add the results and thus eliminate ε. Besides we replace $m^2 e^{\mathrm{i} m \varphi}$ by $-\dfrac{\partial^2}{\partial \varphi^2} e^{\mathrm{i} m \varphi}$, use (15) and solve for the separation constant A'.

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[2] Note that in [6], p. 180, p_ϱ^2 has to be replaced by $p_x^2 + p_y^2$.

The final result has the form

$$A'\chi = A'\chi \tag{17}$$

where

$$A' = \frac{\hbar^2}{\mu^2 - v^2} \left\{ -(1 - v^2)\frac{\partial}{\partial\mu}(\mu^2 - 1)\frac{\partial}{\partial\mu} + (\mu^2 - 1)\frac{\partial}{\partial v}(1 - v^2)\frac{\partial}{\partial v} \right\}$$
$$- \hbar^2 \left(\frac{1}{\mu^2 - 1} - \frac{1}{1 - v^2} \right)\frac{\partial^2}{\partial\varphi^2} + 2M\sigma^2 \frac{(1 - v^2)V_1(\mu) - (\mu^2 - 1)V_2(v)}{\mu^2 - v^2}. \tag{18}$$

From the work done by Cordes [7] on separable partial differential equations it follows that the "separation operator" A', the eigenvalue of which is the separation constant A', commutes with the Hamiltonian H. Therefore, as already Coulson [8] pointed out for a special case, the eigenvalue A' of A' has to be used as a further classifying property of a one-particle state besides of the corresponding irreducible representation of the spatial symmetry group and the corresponding one-electron energy ε. A complete set of quantum mechanical constants of the motion which commute with each other is provided by L_z, A', and (of course) H.

A somewhat tedious calculation – which has, in fact, already been performed by Erikson and Hill [9] for the special case of the two-centre Coulomb potential – gives the final result that

$$A' = -L^2 - \hbar^2\sigma^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + 2M\sigma^2 \frac{(1 - v^2)V_1(\mu) - (\mu^2 - 1)V_2(v)}{\mu^2 - v^2}$$
$$= -L^2 - \hbar^2\sigma^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \beta_{\text{pot}} \tag{19}$$

where L^2 is the square of the angular momentum operator $\vec{L}$. Note that the classical constant of the motion β (Eq. 13) is the precise classical analogue of the separation operator A' (Eq. 19). This must be the case as can be already seen by comparing Eqs. (10) and (18).

3. We finally mention some special separable problems and their constants of the motion.

i) The shape of an atomic nucleus may very well be described to be a prolate or oblate spheroid, especially in the case of rare earths [10]. The most simple and widely used one-particle model for nucleons is the spheroidal well model

$$V = \begin{cases} -V_0 & \mu \leqq \mu_0 \\ \infty & \mu > \mu_0 \end{cases} \tag{20}$$

where $\mu = \mu_0$ is the surface of the nucleus. As a consequence, the Hamiltonian commutes with the separation operator

$$A' = -L^2 + \sigma^2(p_x^2 + p_y^2) - 2M\sigma^2 V_0 \quad (\mu \leqq \mu_0). \tag{21}$$

ii) The constant of the motion for the two-centre Coulomb potential

$$V = -Z_1 e^2/r_1 - Z_2 e^2/r_2 \tag{22}$$

Table 1

Prolate spheroidal coordinates
$r_1 = \sigma(\mu + \nu)$ $r_2 = \sigma(\mu - \nu)$
$\varrho = \sigma\sqrt{(\mu^2 - 1)(1 - \nu^2)}$ $z = \sigma\mu\nu$
$r^2 = \sigma^2(\mu^2 + \nu^2 - 1)$

Separable potential energy $V = \dfrac{V_1(\mu) + V_2(\nu)}{\mu^2 - \nu^2}$	$V_1(\mu)$	$V_2(\nu)$	Contribution to Separation operator $\dfrac{(1 - \nu^2)\,V_1(\mu) - (\mu^2 - 1)\,V_2(\nu)}{\mu^2 - \nu^2}$
$\dfrac{1}{r_1} = \dfrac{1}{\sigma(\mu + \nu)}$	$\dfrac{\mu}{\sigma}$	$-\dfrac{\nu}{\sigma}$	$\dfrac{1}{\sigma}\dfrac{z_1}{r_1}$
$\dfrac{1}{r_2} = \dfrac{1}{\sigma(\mu - \nu)}$	$\dfrac{\mu}{\sigma}$	$\dfrac{\nu}{\sigma}$	$\dfrac{1}{\sigma}\dfrac{z_2}{r_2}$
$r^2 = \sigma^2(\mu^2 + \nu^2 - 1)$	$\sigma^2\mu^2(\mu^2 - 1)$	$\sigma^2\nu^2(1 - \nu^2)$	ϱ^2
$\dfrac{1}{r_1 \cdot r_2} = \dfrac{1}{\sigma^2(\mu^2 - \nu^2)}$	$\dfrac{1}{2\sigma^2}$	$\dfrac{1}{2\sigma^2}$	$-\dfrac{\cos\gamma}{2\sigma^2}$
$\dfrac{1}{\varrho^2} = \dfrac{1}{\sigma^2(\mu^2 - 1)(1 - \nu^2)}$	$\dfrac{1}{\sigma^2(\mu^2 - 1)}$	$\dfrac{1}{\sigma^2(1 - \nu^2)}$	$\dfrac{1 - r^2/\sigma^2}{\varrho^2}$

was analyzed by Erikson and Hill [9] and turned out to be

$$A' = -L^2 + \sigma^2(p_x^2 + p_y^2) - 2Me^2\sigma(Z_1\cos\theta_1 - Z_2\cos\theta_2). \tag{23}$$

Later on, Coulson and Joseph [8] superposed the two-centre Coulomb potential and a harmonic oscillator potential kr^2:

$$V = -Z_1 e^2/r_1 - Z_2 e^2/r_2 + kr^2 \tag{24}$$

The constant of the motion for this case,

$$A' = -L^2 + \sigma^2(p_x^2 + p_y^2) - 2Me^2\sigma(Z_1\cos\theta_1 - Z_2\cos\theta_2) + 2M\sigma^2 k\varrho^2 \tag{25}$$

is an outgrowth of the superposition of separable potentials according to Eqs. (13) and (19); details are to be found in Table 1.

iii) The superposition of a two-centre Coulomb potential $-Z_1/r_1 - Z_2/r_2$ and a potential $-Q/(r_1 r_2)$

$$V = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{Q}{r_1 \cdot r_2} \tag{26}$$

(atomic units in (26)) has found applications in the natural spin orbital analysis of small diatomic molecules [12]. The resulting constant of the motion is [11]:

$$-A' = L^2 - \sigma^2(p_x^2 + p_y^2) + R(Z_1\cos\theta_1 - Z_2\cos\theta_2) + Q\cos\gamma \tag{27}$$

where the third term comes from the two-centre Coulomb potential and the last one from $Q/(r_1 \cdot r_2)$ (compare Table 1).

iv) Teller [13] recently suggested the use of a separable potential energy of the form

$$V \sim \frac{a_{00} + a_{10}\mu + a_{01}\nu + a_{20}\mu^2 + a_{02}\nu^2}{\mu^2 - \nu^2} \tag{28}$$

in an effective one-electron Schrödinger equation for electrons in a diatomic molecule. It is more general than the potential energy (26) because of the quadratic terms $a_{20}\mu^2$ and $a_{02}\nu^2$. Identifying

$$\begin{aligned}
V_1(\mu) &= \tfrac{1}{2}a_{00} + a_{10}\mu + a_{20}\mu^2 \\
V_2(\nu) &= \tfrac{1}{2}a_{00} + a_{01}\nu + a_{02}\nu^2
\end{aligned} \tag{29}$$

we get, according to (19),

$$A' = -L^2 - \hbar^2 \sigma^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \tag{30}$$

$$+ 2M\sigma^2 \frac{(1-\nu^2)(a_{00}/2 + a_{10}\mu + a_{20}\mu^2) + (\mu^2 - 1)(a_{00}/2 + a_{01}\nu + a_{02}\nu^2)}{\mu^2 - \nu^2} .$$

It is, however, difficult to give a simple interpretation of this separation constant.

Cylindrically Symmetrical Potentials Separable in Parabolic Coordinates

1. Parabolic coordinates are as usually defined by

$$\xi = r + z \quad \eta = r - z \quad \varphi \tag{31}$$

and are related to (circular) cylinder coordinates ϱ, φ, z by

$$\varrho = \sqrt{\xi\eta} \quad z = \frac{\xi - \eta}{2} \quad \varphi = \varphi . \tag{32}$$

The most general cylindrically symmetrical potential energy V for which the Schrödinger Eq. (3) separates in parabolic coordinates is of the form

$$V(\xi, \eta) = \frac{V_1(\xi) + V_2(\eta)}{\xi + \eta} \tag{33}$$

according to Eisenhart [4] or Morse and Feshbach [5, p. 660].

Let us first construct a classical constant of the motion before treating the Schrödinger Eq. (3) with the potential energy (33). The canonical momenta are

$$p_\xi = \frac{M}{4\xi}(\xi + \eta)\dot{\xi} = \frac{\partial S_0}{\partial \xi}$$

$$p_\eta = \frac{M}{4\eta}(\xi + \eta)\dot{\eta} = \frac{\partial S_0}{\partial \eta} \tag{34}$$

$$p_\varphi = M\xi\eta\dot{\varphi} \quad = \frac{\partial S_0}{\partial \varphi} .$$

The Hamilton-Jacobi-equation separates with the ansatz

$$S_0 = p_\varphi \cdot \varphi + S_1(\xi) + S_2(\eta) \tag{35}$$

giving (according to Landau and Lifschitz [6, p. 177])

$$2\xi p_\xi^2 + \frac{p_\varphi^2}{2\xi} + M(V_1(\xi) - E\xi) = \quad \beta$$

$$2\eta p_\eta^2 + \frac{p_\varphi^2}{2\eta} + M(V_2(\eta) - E\eta) = -\beta. \qquad (36)$$

Eliminating E from Eq. (36), we obtain for β:

$$\beta = \frac{2\xi\eta}{\xi+\eta}(p_\xi^2 - p_\eta^2) + \frac{\eta-\xi}{2\xi\eta} p_\varphi^2 + M \frac{\eta V_1(\xi) - \xi V_2(\eta)}{\xi+\eta}. \qquad (37)$$

Only the last term of the right side of (37) depends on the potential energy (33).

A short calculation shows that the first sum is equal to minus the z-component of the vector $\vec{p} \times \vec{L}$, where $\vec{L} = (L_x, L_y, L_z)$ is the angular momentum $\vec{r} \times \vec{p}$. We therefore obtain

$$\beta = -(p_x L_y - p_y L_x) + M \frac{\eta V_1(\xi) - \xi V_2(\eta)}{\xi+\eta}. \qquad (38)$$

2. The Schrödinger Eq. (3) for the potential energy (33) separates with the ansatz

$$\chi(\xi, \eta, \varphi) = X(\xi)\, Y(\eta)\, e^{im\varphi}. \qquad (39)$$

The separated equations are

$$\left\{ -\hbar^2 \left(2 \frac{\partial}{\partial \xi} \left(\xi \frac{\partial}{\partial \xi} \right) - \frac{m^2}{2\xi} \right) + M(V_1(\xi) - E\xi) - A \right\} X(\xi) = 0$$

$$\left\{ -\hbar^2 \left(2 \frac{\partial}{\partial \eta} \left(\eta \frac{\partial}{\partial \eta} \right) - \frac{m^2}{2\eta} \right) + M(V_2(\eta) - E\eta) + A \right\} Y(\eta) = 0. \qquad (40)$$

We now repeat the calculation which led from Eqs. (16) to (17) and obtain from (40):

$$A\chi = A\chi, \qquad (41)$$

the separation operator A being equal to

$$A = \frac{\hbar^2}{\xi+\eta} \left\{ -2\eta \frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} + 2\xi \frac{\partial}{\partial \eta} \eta \frac{\partial}{\partial \eta} \right\} + \hbar^2 \frac{\eta-\xi}{2\xi\eta} \frac{\partial^2}{\partial \varphi^2}$$

$$+ M \frac{\eta V_1(\xi) - \xi V_2(\eta)}{\xi+\eta}. \qquad (42)$$

Note that again this separation operator is the quantum mechanical analogue of the separation constant β (Eq. (37)) for the Hamilton-Jacobi equation.

A very tedious calculation (which is omitted) shows that the first term in (42) is equal to the operator

$$A_z = \frac{1}{2} \sum_{j=1}^{3} (L_{3j} p_j - p_j L_{j3}) = \frac{1}{2} (L_{31} p_1 - p_1 L_{13} + L_{32} p_2 - p_2 L_{23})$$

$$= z(p_x^2 + p_y^2) - \frac{1}{2} p_z(p_x x + x p_x + y p_y + p_y y) \qquad (43)$$

where
$$L_{ij} = x_i p_j - x_j p_i$$

is the antimetric tensor operator of angular momentum.

The operator A evidently is the quantum mechanical equivalent of the symmetrized classical expression (38).

We therefore obtain the final result that the separation operator A is equal to

$$A = A_z + M \frac{\eta V_1(\xi) - \xi V_2(\eta)}{\xi + \eta} \tag{44}$$

with A_z defined in Eq. (43).

3. Again we mention some special separable potentials and the resulting constants of the motion.

i) The potential energy

$$V = -\frac{Ze^2}{r} = -\frac{2Ze^2}{\xi + \eta} \tag{45}$$

of a particle with mass M and charge $-e$ in the field of a positive charge Ze (Kepler problem) gives rise to the constant of motion

$$\beta = -(p_x L_y - p_y L_x) + M Ze^2 \frac{z}{r} \tag{46}$$

after the identification $V_1(\xi) = V_2(\eta) = -Ze^2$.

This is the z-component of the famous Runge-Lenz vector

$$-(\vec{p} \times \vec{L}) + M Ze^2 \frac{\vec{r}}{r} \tag{47}$$

pointing in the direction of the major axis of the Kepler ellipse. From (44) its quantum mechanical analogue is derived and turns out to be

$$A = -\frac{1}{2} \sum_{j=1}^{3} (p_j L_{j3} - L_{3j} p_j) + M Ze^2 \frac{z}{r} . \tag{48}$$

This is the z-component of the quantum mechanical Lenz-Pauli-vector. Its eigenvalue in the eigenstate $|STm\rangle$ with parabolic quantum numbers S, T, m is given by

$$A = \frac{S - T}{S + T + |m| + 1} Ze^2 M \tag{49}$$

according to Landau-Lifschitz [14, p. 133].

ii) If a homogeneous electric field with strength F in the direction of the positive z-axis is superimposed to the field of an atomic nucleus with charge Ze, the resulting potential energy of an electron with charge $-e$ is

$$-\frac{Ze^2}{r} + eFz . \tag{50}$$

The resulting constant of the motion now is

$$\beta = -(p_x L_y - p_y L_x) + M Ze^2 \frac{z}{r} + \frac{M}{2} eF \varrho^2 \tag{51}$$

in classical mechanics.

The quantum mechanical separation operator is, according to (44), (50), and Table 2

$$A = -\frac{1}{2} \sum_{j=1}^{3} (p_j L_{j3} - L_{3j} p_j) + MZe^2 \frac{z}{r} + \frac{M}{2} eF\varrho^2 . \qquad (52)^3$$

In Fig. 2, energy E and separation constant $-A$ of several excited states of (50) with $Z = 1$ are given as a function of the electric field strength F. The method of calculation used was the reduction of the system of two differential eigenvalue Eqs. (40) to a system of two coupled algebraic eigenvalue equations. This system was subjected to a Newton-Raphson-procedure described in the appendix of [15].

Two features of Fig. 2 are essential.

1) $-A$ is a slowly decreasing, almost linear function of F which is well approximated by the expectation value

$$(STm | -A | STm) = \frac{T - S}{S + T + |m| + 1} - \frac{1}{2} F(STm | \varrho^2 | STm) \qquad (53)$$

calculated with parabolic hydrogenic functions $|STm)$. These functions have recently been given as linear combinations of spherical hydrogenic functions $|nlm)$ [16a, b].

2) The state $|040)$ of type σ^+ $(C_{\infty v})$ crosses the states $|300)$, $|210)$, and $|120)$ of equal type σ^+ $(C_{\infty v})$ with regard to energy. This is no violation of the non-crossing rule since the full symmetry $C_{\infty v} \times \{A\}$ of (50) has to be taken into account and a complete classification is given by (γ, A) where γ is an irreducible representation of $C_{\infty v}$ and A the separation constant. The values of the separation constant A for all these states are well separated.

iii) We finally mention the problem

$$\left\{ -\frac{\hbar^2}{2M} \Delta - e^2 Z/r + \frac{C}{\varrho^2} \right\} \chi = \varepsilon \chi \qquad (\varrho^2 = x^2 + y^2) \qquad (54)$$

recently solved by Hartmann [17].

(54) is separable both in spherical and in parabolic coordinates. Separability in spherical coordinates and spatial cylinder symmetry give rise to the two constants of motion

$$L^2 + \frac{2MC}{\sin^2 \vartheta} , \qquad (55a)$$

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi} . \qquad (55b)$$

Separability in parabolic coordinates comes from the fact that

$$\frac{1}{\varrho^2} = \frac{1}{\xi \cdot \eta} = \frac{\dfrac{1}{\xi} + \dfrac{1}{\eta}}{\xi + \eta} . \qquad (56)$$

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[3] For another derivation of the Stark-effect generalization of the Lenz-Pauli-vector see: Redmond, P. J.: Physic. Rev. **133** B, 1352 (1964).

Table 2

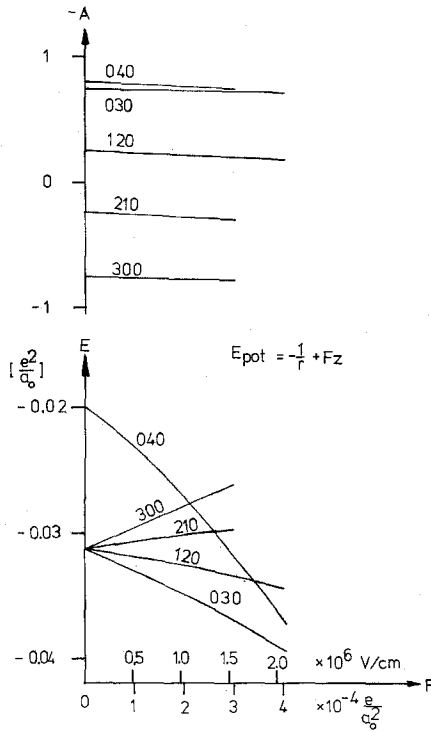| Circular parabolic coordinates			
$\xi = r + z \quad \eta = r - z \quad \varphi$			
$\varrho^2 = \xi\eta$			
Separable potential energy $V = \dfrac{V_1(\xi) + V_2(\eta)}{\xi + \eta}$	$V_1(\xi)$	$V_2(\eta)$	Contribution to separation operator $\dfrac{\eta V_1(\xi) - \xi V_2(\eta)}{\xi + \eta}$
$\dfrac{1}{r}$	1	1	$-\dfrac{z}{r}$
$\dfrac{z}{r}$	ξ	$-\eta$	$\dfrac{\varrho^2}{r}$
z	$\dfrac{\xi^2}{2}$	$-\dfrac{\eta^2}{2}$	$\dfrac{\varrho^2}{2}$
$\dfrac{1}{\varrho^2}$	$\dfrac{1}{\xi}$	$\dfrac{1}{\eta}$	$-\dfrac{2z}{\varrho^2}$

Fig. 2. Energy F and separation constant A as functions of electric field strength F for several electronic states $ST0$ of type σ^+ $(m = 0)$. The operator of potential energy is $-\dfrac{1}{r} + Fz$

According to (44) and Table 2, it gives rise to the additional third constant of motion

$$A = -\frac{1}{2} \sum_{j=1}^{3} (p_j L_{j3} - L_{3j} p_j) + M Z e^2 \frac{z}{r} - M C \frac{2z}{\varrho^2} . \qquad (55c)$$

So the number of independent constants of the motion is even greater than in the Stark effect problem ii) and equal to the corresponding number in the Zeeman effect problem.

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