

Hybrid Orbitals and the Runge-Lenz Vector

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Abstracts

Matrix elements of the Runge-Lenz vector \mathbf{A} are presented for those linear combinations of degenerate hydrogenic functions often referred to as hybrid orbitals. The uncertainties in the components of \mathbf{A} for each type of wave-function are related to the distribution of classical Kepler orbits corresponding to each function. Matrix elements of \mathbf{A} with respect to radially nodeless Slater functions are presented, as these functions are often used as a basis set in atomic and molecular calculations. The properties of \mathbf{A} for a piecewise Coulombic central field are discussed in relation to the description of penetrating orbits in the old quantum theory. Simultaneous eigenfunctions of \mathbf{A} and the Hamiltonian cannot be chosen for the piecewise Coulombic field because of a discontinuity in the radial derivative of the potential energy.

On présente des éléments de la matrice représentant le vecteur de Runge-Lenz \mathbf{A} dans une base consistant d'orbitales hybridées de fonctions hydrogénoïdes. Les mesures d'indétermination des composantes de \mathbf{A} pour chaque type de fonction d'onde sont associées à la distribution des orbites de Kepler classiques correspondant à chaque fonction. On présente aussi des éléments de la matrice de \mathbf{A} par rapport à des fonctions de Slater sans nœuds. Les propriétés de \mathbf{A} pour un champ Coulombien central par morceaux sont discutées par rapport à la description des orbites pénétrantes dans la vieille théorie quantique. Il n'est pas possible de choisir des fonctions propres simultanées de \mathbf{A} et du Hamiltonien, à cause d'une discontinuité dans la dérivée radiale de l'énergie potentielle.

Matrizelemente des Runge-Lenz'schen Vektors \mathbf{A} mit Rücksicht auf von entarteten Wasserstofffunktionen konstruierte Hybridorbitale werden angegeben. Die Unbestimmtheiten in den Komponenten von \mathbf{A} für jeden Typ von Wellenfunktionen sind mit der jeder Funktion entsprechenden Verteilung der klassischen Keplerbahnen verbunden. Matrizelemente von \mathbf{A} werden auch mit Rücksicht auf knotenlose, radielle Slaterfunktionen angegeben. Die Eigenschaften von \mathbf{A} für ein stückweise Coulombisches Zentralfeld werden in Bezug auf die Beschreibung von penetrierenden Bahnen in der alten Quantentheorie diskutiert. Gleichzeitige Eigenfunktionen von \mathbf{A} und vom Hamiltonoperator können für das stückweise Coulombische Feld wegen einer Diskontinuität in der radiellen Ableitung der potentiellen Energie nicht gewählt werden.

It has been known for some time that the "accidental" degeneracy associated with the nonrelativistic description of the bound states of hydrogenic atoms may be related [1, 2] to the invariance of the Hamiltonian with respect to the four-dimensional orthogonal symmetry group O_4 . Alternatively, the degeneracy may be related [1, 3] to the existence of a vector constant of motion in addition to the orbital angular momentum vector. This vector is called [4] the Runge-Lenz vector \mathbf{A} and may be written [1-3]* as

$$\mathbf{A} = 1/2\{(\mathbf{p} \times \mathbf{L}) - (\mathbf{L} \times \mathbf{p})\} - \mathbf{Pr}/r \quad (1)$$

* Several definitions of \mathbf{A} exist which differ by multiplicative factors. We follow Englefield [2], whose \mathbf{A} has dimensions of momentum. The \mathbf{A} of Bander and Itzykson [1] has the same sign but dimensions of charge squared, while that of Pauli [3] is of opposite sign and dimensionless.

where \mathbf{p} is the linear momentum operator, $\hbar\mathbf{L}$ is the orbital angular momentum operator (\hbar is Planck's constant divided by 2π), \mathbf{r} is the electron radius vector, and P is a constant $\mu Z e^2/\hbar$ with the dimensions of momentum where μ is the reduced mass, Z is the atomic number, and e is the magnitude of electron charge. The constant P may also be written as $Z\hbar/a_H$, in which $a_H = \hbar^2/\mu e^2 = (m/\mu)a_0$ where m is the electron mass and a_0 is the Bohr radius for infinite nuclear mass. Classically, the vector \mathbf{A} lies along the major axis of an elliptical orbit and has a magnitude equal to P times the eccentricity of the orbit. For the sign convention in Eq. (1), \mathbf{A} points in the direction of the perihelion of the orbit.

The Runge-Lenz vector has attracted considerable attention in recent years because of its usefulness in approximately describing [5-12] the dynamical symmetry in two-electron atoms. Specifically, configuration mixing coefficients for doubly excited states have been obtained [8-12] group-theoretically by considering a basis which is diagonal in the square of the difference of the Runge-Lenz vectors of the electrons and subject to conservation of parity and of orbital and spin angular momenta. Other applications have included the evaluation [13] of Coulomb integrals with respect to hydrogenic wave-functions and the determination [14] of a "hidden" constant of motion for the two-center Coulomb problem. Some developments in the analysis of the dynamical symmetries of classical systems included the demonstration [15, 16] of the existence of a Runge-Lenz-type vector for all spherically symmetric single-particle potentials in three dimensions.

The basic commutation relationships involving \mathbf{A} , \mathbf{L} , and the hydrogenic Hamiltonian \mathcal{H} have been given by several authors [1-3] and are

$$\begin{aligned} [A_j, A_k] &= -2i\epsilon_{jkl}\mu L_l \mathcal{H} \\ [L_j, A_k] &= i\epsilon_{jkl}A_l \\ [L_j, L_l] &= i\epsilon_{jkl}L_l \\ [\mathcal{H}, A_j] &= [\mathcal{H}, L_j] = 0 \\ \mathbf{A} \cdot \mathbf{L} &= \mathbf{L} \cdot \mathbf{A} = 0 \end{aligned} \quad (2)$$

where the factor ϵ_{jkl} is the Levi-Civita tensor.*

The vector \mathbf{A} has been used to derive matrix elements of the position vector \mathbf{r} without explicitly using radial wave-functions. The key result, obtained [2] by Englfield using a hypervirial relationship, is

$$4\mu E_n \langle nl || \mathbf{r} || nl' \rangle = 3\hbar \langle nl || \mathbf{A} || nl' \rangle \quad (3)$$

in which the energy eigenvalues E_n are

$$E_n = \frac{-\mu Z^2 e^4}{2\hbar^2 n^2} = \frac{-P^2}{2\mu n^2} \quad (4)$$

* The tensor ϵ_{jkl} equals zero if any two subscripts are equal, equals +1 if jkl represents an even permutation of xyz , and equals -1 if jkl represents an odd permutation of xyz .

The double bars in Eq. (3) denote reduced matrix elements related to matrix elements by the Wigner-Eckart theorem, which for complex components may be written

$$\langle nlm|l''m''|nl'm'\rangle = (-1)^{l-m}\langle nl||l''||nl'\rangle \bar{V}\begin{pmatrix} l & l' & l'' \\ -m & m' & m'' \end{pmatrix} \quad (5)$$

where \bar{V} is the vector coupling coefficient of Fano and Racah [17]. Alternatively, the use of Griffith's V coefficients [18] for real components yields

$$\langle \alpha\Gamma M_\Gamma|\Gamma''M''_\Gamma|\alpha'\Gamma'M'_\Gamma\rangle = \langle \alpha\Gamma||\Gamma''||\alpha'\Gamma'\rangle V\begin{pmatrix} \Gamma & \Gamma' & \Gamma'' \\ M_\Gamma & M'_\Gamma & M''_\Gamma \end{pmatrix} \quad (6)$$

in which the quantum numbers α , Γ , and M_Γ are analogous to n , l , and m , respectively.

Since \mathbf{A} commutes with the hydrogenic Hamiltonian, the matrix of \mathbf{A} is diagonal in the principal quantum number n , and Eq. (3) cannot be used to obtain matrix elements of \mathbf{r} between states of different n . The fact that matrix elements of \mathbf{A} between states of the same n are simply proportional to those of \mathbf{r} might make it seem that there is little use in discussing the former except as a route to the latter. However, as we shall show, it is the special property of \mathbf{A} being diagonal in n which makes it useful for an analysis of the properties of hydrogenic hybrid orbitals.

Pauli showed [3] that the eigenstates for a hydrogenic atom in a weak electric field may be chosen as simultaneous eigenstates of the components of \mathbf{A} and \mathbf{L} parallel to the field. For $n = 2$ these states are the pair of functions often described as digonal sp hybrids together with the pair of p functions with $M_l = \pm 1$. Choosing z as the field direction, these four functions are eigenstates of A_z , but not of A_x and A_y , as the latter operators mix the digonal hybrids with $2p_x$ and $2p_y$ functions, respectively. The operation of A_z on the familiar real $n = 2$ functions gives

$$\begin{aligned} A_z|2s\rangle &= (P/2)|2p_z\rangle \\ A_z|2p_x\rangle &= 0 \\ A_z|2p_y\rangle &= 0 \\ A_z|2p_z\rangle &= (P/2)|2s\rangle \end{aligned} \quad (7)$$

with similar results for A_x and A_y . Thus, A_z simply interchanges the functions $2s$ and $2p_z$. The reduced matrix element* $\langle 2s||\mathbf{A}||2p\rangle$ is $3^{1/2}P/2$. As given by Pauli, but using Englefield's sign convention [2], the eigenvalues of A_z are $\pm P/2$ for the digonal hybrids $2^{-1/2}[|2s\rangle \pm |2p_z\rangle]$ and zero for $2p_+$ and $2p_-$ (or equivalently for $2p_x$ and $2p_y$). In addition, each digonal hybrid is connected to $2p_x$ by a matrix

* The positive sign for $\langle nl||\mathbf{A}||nl'\rangle$ corresponds, using Eq. (3), to a negative sign for $\langle nl||\mathbf{r}||nl'\rangle$. This implies a choice of radial phases such that the lobe closest to the nucleus has the same sign, say positive, for all states. Thus the outer lobe of $|2s\rangle$ is negative, making the density associated with the digonal hybrid $2^{-1/2}[|2s\rangle + |2p_z\rangle]$ point along the negative z axis.

element of A_x equaling $8^{-1/2}P$ and to $2p_y$ by a matrix element of A_y equaling $8^{-1/2}P$.

A trigonal set of sp^2 functions for $n = 2$ may be defined by

$$\begin{aligned}\psi_1 &= 3^{-1/2}[[2s] + 2^{1/2}[2p_x]] \\ \psi_2 &= 3^{-1/2}[[2s] - 2^{-1/2}[2p_x] + (3/2)^{1/2}[2p_y]] \\ \psi_3 &= 3^{-1/2}[[2s] - 2^{-1/2}[2p_x] - (3/2)^{1/2}[2p_y]]\end{aligned}\quad (8)$$

In Table I we present the matrices of A_x , A_y , and A_z with respect to the functions in Eq. (8) together with $\psi_4 = |2p_z\rangle$. The diagonal elements are the direction cosines of Eq. (8) multiplied by the constant $2^{1/2}P/3$ and are components of the vector expectation value

TABLE I. Matrix elements^a of \mathbf{A} in sp^2 basis^b for $n = 2$.

	ψ_1	ψ_2	ψ_3	ψ_4	
A_x	ψ_1	$(8/3)^{1/2}$	$6^{-1/2}$	$6^{-1/2}$	0
	ψ_2	$6^{-1/2}$	$-(2/3)^{1/2}$	$-(2/3)^{1/2}$	0
	ψ_3	$6^{-1/2}$	$-(2/3)^{1/2}$	$-(2/3)^{1/2}$	0
	ψ_4	0	0	0	0
A_y	ψ_1	0	$2^{-1/2}$	$-2^{-1/2}$	0
	ψ_2	$2^{-1/2}$	$2^{1/2}$	0	0
	ψ_3	$-2^{-1/2}$	0	$-2^{1/2}$	0
	ψ_4	0	0	0	0
A_z	ψ_1	0	0	0	1
	ψ_2	0	0	0	1
	ψ_3	0	0	0	1
	ψ_4	1	1	1	0

^a In units of $12^{-1/2}P$.

^b Basis defined by Eq. (8) together with $\psi_4 = |2p_z\rangle$.

$$\langle\psi|\mathbf{A}|\psi\rangle = \langle\psi|A_x|\psi\rangle\mathbf{i} + \langle\psi|A_y|\psi\rangle\mathbf{j} + \langle\psi|A_z|\psi\rangle\mathbf{k}\quad (9)$$

where \mathbf{i} , \mathbf{j} , and \mathbf{k} are unit vectors in the x , y , and z directions, respectively. Thus, as indicated by Eq. (3), the expectation value of \mathbf{A} lies antiparallel to the mean position of the charge density. The nonvanishing of Eq. (9) for the pair of digonal functions and for ψ_1 , ψ_2 , and ψ_3 indicates that each of these hybrid functions corresponds to a set of classical elliptical orbits whose mean \mathbf{A} value equals the expectation value.

Similar properties hold for the set of four $n = 2$ sp^2 hybrid functions

$$\begin{aligned}\psi_a &= 1/2[[2s] + [2p_x] + [2p_y] + [2p_z]] \\ \psi_b &= 1/2[[2s] - [2p_x] - [2p_y] + [2p_z]] \\ \psi_c &= 1/2[[2s] - [2p_x] + [2p_y] - [2p_z]] \\ \psi_d &= 1/2[[2s] + [2p_x] - [2p_y] - [2p_z]]\end{aligned}\quad (10)$$

for which we present the matrix elements of A_x , A_y , and A_z in Table II.

TABLE II. Matrix elements^a of \mathbf{A} in sp^3 basis^b for $n = 2$.

		ψ_a	ψ_b	ψ_c	ψ_d
A_x	ψ_a	1	0	0	1
	ψ_b	0	-1	-1	0
	ψ_c	0	-1	-1	0
	ψ_d	1	0	0	1
A_y	ψ_a	1	0	1	0
	ψ_b	0	-1	0	-1
	ψ_c	1	0	1	0
	ψ_d	0	-1	0	-1
A_z	ψ_a	1	1	0	0
	ψ_b	1	1	0	0
	ψ_c	0	0	-1	-1
	ψ_d	0	0	-1	-1

^a Basis defined by Eq. (10).

^b In units of $P/4$.

The spread σ associated with the i th component of \mathbf{A} is given by

$$\sigma^2(A_i) = \langle \psi | A_i^2 | \psi \rangle - |\langle \psi | A_i | \psi \rangle|^2 \tag{11}$$

For the sp^2 hybrids in Eq. (8),

$$\begin{aligned} \langle \psi_1 | A_x^2 | \psi_1 \rangle &= P^2/4 \\ \langle \psi_2 | A_x^2 | \psi_2 \rangle &= \langle \psi_3 | A_x^2 | \psi_3 \rangle = P^2/8 \\ \langle \psi_1 | A_y^2 | \psi_1 \rangle &= P^2/12 \\ \langle \psi_2 | A_y^2 | \psi_2 \rangle &= \langle \psi_3 | A_y^2 | \psi_3 \rangle = P^2/6 \\ \langle \psi_i | A_z^2 | \psi_i \rangle &= P^2/12 \text{ (for } i = 1-3) \end{aligned} \tag{12}$$

Combining Eq. (12) with matrix elements of \mathbf{A} in Table I yields: $\sigma(A_x)$ values of $P/6$ for ψ_1 and $(5/72)^{1/2}P$ for ψ_2 and ψ_3 ; $\sigma(A_y)$ values of $12^{-1/2}P$ for ψ_1 and $6^{-1/2}P$ for ψ_2 and ψ_3 ; and $\sigma(A_z)$ values of $12^{-1/2}P$ for ψ_i , where $i = 1-3$. The smallest of these values is $\sigma(A_x)$ for ψ_1 , indicating simply that the orientation of the function in Eq. (8) with respect to the Cartesian axes places ψ_1 along the x axis. The functions ψ_1 , ψ_2 , and ψ_3 are equivalent by symmetry and must have identical properties. However, it is significant that $\sigma(A_y)$ and $\sigma(A_z)$ for ψ_1 are each larger by a factor of $3^{1/2}$ than $\sigma(A_x)$ for ψ_1 , indicating that ψ_1 is closer to being an eigenfunction of A_x than of A_y or A_z . Since it can easily be shown from the “interchange” properties in Eq. (7) that *any* superposition of s and p functions for $n = 2$ is an eigenfunction of the square of the component of \mathbf{A} parallel to the direction of the mean charge density, it follows that ψ_1 is an eigenfunction of A_x^2 , although not of A_x .

By contrast, the sp hybrids, which are eigenfunctions of A_z , are characterized by $\sigma(A_z) = 0$ and $\sigma(A_x) = \sigma(A_y) = 8^{-1/2}P$. The latter follows from the fact that the mean values of A_x^2 and A_y^2 are $P^2/8$ while the mean values of A_x and A_y are zero. Thus, the hybrids $2^{-1/2}[[2s] \pm [2p_z]]$ correspond to sets of elliptical orbits having $A_z = \pm P/2$, respectively, but with a spread of A_x and A_y values. Specifically, the magnitude of A_z for these hybrids is $2^{-1/2}$ times that of \mathbf{A} itself, as it is for an elliptical orbit of any orientation that places the major axis at an angle of 45° to the z axis. If, in addition, the plane of the orbit contains the z axis, then L_z is zero and the correspondence is even closer.

For each of the four sp^2 hybrid $n = 2$ functions in Eq. (10)

$$\langle \psi | A_x^2 | \psi \rangle = \langle \psi | A_y^2 | \psi \rangle = \langle \psi | A_z^2 | \psi \rangle = P^2/8 \quad (13)$$

and

$$|\langle \psi | A_x | \psi \rangle| = |\langle \psi | A_y | \psi \rangle| = |\langle \psi | A_z | \psi \rangle| = P/4 \quad (14)$$

so that

$$\sigma(A_x) = \sigma(A_y) = \sigma(A_z) = P/4 \quad (15)$$

meaning that the spread in each component of \mathbf{A} equals the magnitude of the mean value of that component.

The properties of states with $n > 2$ may be illustrated by the operation of \mathbf{A} on the familiar real eigenstates of L^2 for $n = 3$:

$$A_x |3p_y\rangle = A_y |3p_x\rangle = 3^{-1}P |3d_{xy}\rangle \quad (16a)$$

with similar relationships involving x, z and y, z :

$$\begin{aligned} A_x |3p_x\rangle &= (8/27)^{1/2}P |3s\rangle - 27^{-1/2}P |3d_{3z^2-r^2}\rangle \\ &\quad + 3^{-1}P |3d_{x^2-y^2}\rangle \end{aligned} \quad (16b)$$

with a change in sign of the last term for $A_y |3p_y\rangle$; and

$$A_z |3p_z\rangle = (8/27)^{1/2}P |3s\rangle + (4/3)^{1/2}P |3d_{3z^2-r^2}\rangle \quad (16c)$$

The results are also presented as the matrix elements in Table III. Reduced matrix elements for use in Eq. (6) with coupling coefficients for the O_h group are

$$\begin{aligned} \langle 3s(a_{1g}) || \mathbf{A}(t_{1u}) || 3p(t_{1u}) \rangle &= 8^{1/2}P/3 \\ \langle 3p(t_{1u}) || \mathbf{A}(t_{1u}) || 3d(e_g) \rangle &= -2P/2 \\ \langle 3p(t_{1u}) || \mathbf{A}(t_{1u}) || 3d(t_{2g}) \rangle &= -6^{1/2}P/3 \end{aligned} \quad (17)$$

The simultaneous eigenfunctions of A_z and L_z are the spd linear hybrids with $M_L = 0$, the pd linear hybrids with $M_L = \pm 1$, and the unmixed d functions with $M_L = \pm 2$. The properties of \mathbf{A} with respect to hybrid $n = 3$ functions are similar to those we have discussed for $n = 2$, so that the spread in the component of \mathbf{A} parallel to the direction of an sp^3d^2 hybrid is small compared to the spread in perpendicular components.

TABLE III. Matrix elements^a of **A** for $n = 3$.

		s	$d_{3z^2-r^2}$	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
A_x	p_x	$(8/3)^{1/2}$	$-3^{-1/2}$	1	0	0	0
	p_y	0	0	0	1	0	0
	p_z	0	0	0	0	1	0
A_y	p_x	0	0	0	1	0	0
	p_y	$(8/3)^{1/2}$	$-3^{-1/2}$	-1	0	0	0
	p_z	0	0	0	0	0	1
A_z	p_x	0	0	0	0	1	0
	p_y	0	0	0	0	0	1
	p_z	$(8/3)^{1/2}$	$(4/3)^{1/2}$	0	0	0	0

^a In units of $P/3$.

The hybrid functions used to describe bonding in molecules are usually taken not as superpositions of hydrogenic functions but rather of atomic central-field functions. The matrix of **A** is not diagonal in the principal quantum number n for such functions, which are frequently determined by a self-consistent field (SCF) procedure involving an expansion in either a Slater or Gaussian basis set. A Slater s function may be written

$$|ns\rangle = \left[\frac{(2\alpha)^{2n+1}}{4\pi(2n)!} \right]^{1/2} r^{n-1} e^{-\alpha r} = N_s r^{n-1} e^{-\alpha r} \tag{18}$$

so that

$$A_z |ns\rangle = N_s \left[(\hbar\alpha - P) - \frac{\hbar(n-1)}{r} \right] r^{n-1} e^{-\alpha r} \cos \theta \tag{19}$$

Since a Slater p_z function may be written

$$|np_z\rangle = \left[\frac{3(2\beta)^{2n+1}}{4\pi(2n)!} \right]^{1/2} r^{n-1} e^{-\beta r} \cos \theta = N_p r^{n-1} e^{-\beta r} \cos \theta \tag{20}$$

we have

$$\begin{aligned} \langle np_z | A_z | n's \rangle &= (4\pi/3) N_s N_p \frac{(n+n'-1)!}{(\alpha+\beta)^{n+n'+1}} \\ &\times [(\hbar\alpha - P)(n+n') - \hbar(n'-1)(\alpha+\beta)] \end{aligned} \tag{21}$$

which is not diagonal in n . For $n' = 1$, the second term in Eqs. (19) and (21) vanishes, while the first term approaches zero as $\hbar\alpha$ approaches $P = \hbar Z/a_H$, the hydrogenic value of $\hbar\alpha$ for $n' = 1$. Thus, as expected, **A** annihilates a hydrogenic $1s$ function. For $n = n' = 2$ and $\alpha = \beta = Z/2a_H$, $\langle 2p_z | A_z | 2s \rangle$ from Eqs. (21) equals $-3^{1/2}P/4$, as compared to the hydrogenic value of $P/2$. The sign difference arises trivially from the fact that the phase of the Slater $|2s\rangle$ function (18) is positive while that of the corresponding outer lobe of the hydrogenic $|2s\rangle$ function is negative.

The value of $-3^{1/2}P/4$ is unchanged if the Slater $|2s\rangle$ function is Schmidt-orthogonalized to a Slater $|1s\rangle$ function with the same exponent as the $|2s\rangle$ function, namely $Z/2a_H$. The resulting $|2s\rangle$ function differs from the hydrogenic $|2s\rangle$ function in having its radial node at $3a_H/Z$ instead of $2a_H/Z$ and by having a normalization constant larger by a factor of $12^{1/2}/3$. While a diagonal hydrogenic hybrid $2^{-1/2}[|2s\rangle + |2p_z\rangle]$ is an eigenfunction of both A_z and A_z^2 , with $\sigma(A_z) = 0$, the corresponding Slater hybrid constructed with either the radially nodeless or the orthogonalized $|2s\rangle$ function is not an eigenfunction of either operator but has $\sigma(A_z) = 5^{1/2}P/12$, a value obtained from the matrix elements $\langle 2s|A_z^2|2s\rangle = 7P^2/36$, $\langle 2p_z|A_z^2|2p_z\rangle = P^2/4$, and $\langle 2p_z|A_z|2s\rangle \cong -3^{1/2}P/4$. The expectation value of A_z for the Slater hybrid is also $-3^{1/2}P/4$, smaller in magnitude than the hydrogenic value of $P/2$. While these results are for sp hybrids using single Slater functions, Eq. (21) may be used to evaluate matrix elements of \mathbf{A} with respect to any sp^n hybrids constructed from atomic functions which are superpositions of any number of Slater basis functions.

To obtain matrix elements connecting Slater p and d functions we use

$$A_z|np_z\rangle = \{(\hbar k - P)/3 + \hbar/r - (3 \cos^2 \theta - 1)(2\hbar k + P)/3\} N_p r_{n-1} e^{-\beta r} \quad (22)$$

which is a superposition of radially modified $|ns\rangle$ and $|nd_{3z^2-r^2}\rangle$ functions, or

$$A_x|np_z\rangle = -\{2\hbar k + P\} N_p r^{n-1} e^{-\beta r} \sin \theta \cos \theta \cos \phi \quad (23)$$

which is a modified $|nd_{xy}\rangle$ function; the factor k in Eqs. (22) and (23) equals $[(n-2)/r] - \beta$. The matrix element $\langle n's|A_z|np_z\rangle$ is the same as that given in Eq. (21), while

$$\langle n'd_{xz}|A_x|np_z\rangle = -(4\pi/15) N_p N_d \{2\hbar k + P\} \frac{(n+n')!}{(\beta + \gamma)^{n+n'+1}} \quad (24)$$

where γ is the exponent for $|n'd_{xz}\rangle$ and N_d is the normalization constant $[(15/4\pi)(2\gamma)^{2n'+1}/(2n'!)]^{1/2}$.

Other matrix elements involving $|n'd\rangle$ and $|np\rangle$ functions are readily obtained from Eq. (24) by the use of coupling coefficients. Reduced matrix elements thus obtained from Eqs. (21) or (24) can then be used to scale the matrix elements in Tables I-III to a non-hydrogenic basis.

An interesting example of a central field is the piecewise Coulombic field corresponding to a positive nucleus surrounded by spherical shells of negative charge. This field has been used by McGuire [19] and by Chapman and Lohr [20] in calculating continuum wave-functions and photoionization cross sections. Since the field is Coulombic in each region of space, hydrogenic wave-functions matched at each shell radius form exact solutions of the Schrödinger equation. However, the bound states do not possess the n^2 (excluding spin) hydrogenic degeneracy. It is instructive to examine carefully the commutator $[\mathbf{A}, \mathcal{H}]$ when \mathcal{H} contains a piecewise Coulombic potential energy. We first write

$$\mathbf{A} = \mathbf{A}_1 + \mathbf{A}_2$$

where

$$\mathbf{A}_1 = 1/2[(\mathbf{p} \times \mathbf{L}) - (\mathbf{L} \cdot \mathbf{p})]$$

and

$$\mathbf{A}_2 = -P\mathbf{r}/r$$

Thus,

$$[\mathbf{A}, \mathcal{H}] = [\mathbf{A}_1, T] + [\mathbf{A}_1, V] + [\mathbf{A}_2, T] + [\mathbf{A}_2, V] \quad (26)$$

Since \mathbf{A}_2 and V are multiplicative operators, $[\mathbf{A}_2, V]$ equals zero. If V is a function of r only, then

$$[\mathbf{A}_1, V] = -i(dV/dr)[r^{-1}(\mathbf{r} \cdot \mathbf{p})\mathbf{r} - r\mathbf{p}] \quad (27)$$

From Englefield [2],

$$[\mathbf{A}_2, T] = (i\hbar P/2\mu)\{r^{-3}[\mathbf{r} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{r} + 3i\hbar]\mathbf{r} - 2r^{-1}\mathbf{p}\} \quad (28)$$

For a hydrogenic system $dV/dr = Ze^2/r^2$, so that

$$[\mathbf{A}_1, V] = -[\mathbf{A}_2, T] \quad (29)$$

if P in \mathbf{A}_2 is set equal to $Z\hbar/a_H = Ze^2\mu/\hbar$. The remaining term in Eq. (26), $[\mathbf{A}_1, T]$, equals zero assuming* that it operates on functions which are analytic. Thus, from Eq. (26) the well known result is $[\mathbf{A}, \mathcal{H}] = 0$. For smooth but non-Coulombic central fields Eq. (29) no longer holds, so that $[\mathbf{A}, \mathcal{H}] \neq 0$, meaning that \mathbf{A} is no longer a constant of motion. However, for the piecewise Coulombic field for which $V(r) = -(Z_i^{\text{eff}} e^2/r) + C_i$ in the i th region, where $Z_i^{\text{eff}} e$ is the effective nuclear charge and C_i is the external shielding constant, the commutator $[\mathbf{A}_1, V]$ again equals $-[\mathbf{A}_2, T]$, as in Eq. (29), if P is set equal to $Z_i^{\text{eff}} \hbar/a_H$. The reason is that both commutators are proportional to Z_i^{eff} , so that even though dV/dr in $[\mathbf{A}_1, V]$ is discontinuous, the change is matched by the change in P in $[\mathbf{A}_2, T]$. We know that $[\mathbf{A}, \mathcal{H}]$ cannot be zero for the piecewise Coulombic field, so we must examine the behavior of the commutators at the shell radii. Consider a single negatively charged shell of radius a . The coefficient P in \mathbf{A}_2 has a finite jump discontinuity at $r = a$, so we write

$$P = (e^2\mu/\hbar)[Z_{<}^{\text{eff}}\theta(a-r) + Z_{>}^{\text{eff}}\theta(r-a)] \quad (30)$$

where $\theta(r-a)$ is the Heaviside function†, and $Z_{<}^{\text{eff}} e$ and $Z_{>}^{\text{eff}} e$ are the effective nuclear charges for $r < a$ and $r > a$, respectively. The term in T involving radial

* While $[\mathbf{A}_1, T]$ contains fourth derivatives with respect to Cartesian coordinates, it is easily shown to contain no derivatives higher than the third with respect to the radial coordinate r . As described in [20], not only are the piecewise Coulombic wave-functions and their first derivatives with respect to r continuous at the shell radii, but also their second derivatives are continuous. The jump discontinuities in the third radial derivatives at the shell radii are finite, so that a Dirac δ function does not appear until fourth radial derivatives are taken. As such derivatives do not appear in $[\mathbf{A}_1, T]$, we may still take this commutator to equal zero.

† The function $\theta(x)$ equals zero for $x < 0$ but unity for $x > 0$, so that $d\theta/dx$ equals $\delta(x)$, the Dirac delta function.

derivatives is $-(\hbar^2/2\mu)r^{-2}\partial/\partial r(r^2\partial/\partial r)$, leading to

$$[\mathbf{A}_2, T] = [\text{terms in Eq. (28)}] + (e^2\hbar/2)(\mathbf{r}/r) \\ \times (Z_{<}^{\text{eff}} - Z_{>}^{\text{eff}})\{2\delta(r-a)(r^{-1} + \partial/\partial r) + \delta'(r-a)\} \quad (31)$$

where $\delta(r-a)$ is the Dirac delta function and $\delta'(r-a)$ is its derivative with respect to r . The terms in Eq. (31) which are like Eq. (28), but with the value of P given by Eq. (30), are those which add to $[\mathbf{A}_1, V]$ to give zero. No terms involving $\delta(r-a)$ arise in $[\mathbf{A}_1, V]$, which contains dV/dr but no higher derivatives of V , and none arise* in $[\mathbf{A}_1, T]$ or $[\mathbf{A}_2, V]$. Thus the finite jump discontinuity in dV/dr at $r=a$ introduces a discontinuity in the definition of \mathbf{A}_2 , using Eq. (30), leading to the result that $[\mathbf{A}, \mathcal{H}]$ does not vanish at the shell radius; hence \mathbf{A} is not a constant of motion. It is interesting to note that the penetrating orbits obtained from the old quantum theory [21] for a two-region piecewise Coulombic field are segments of Kepler ellipses in each region. The change in the eccentricity and orientation of these segments, and hence in the value of \mathbf{A} , in passing from one region to the other results in an advancing perihelion and an overall rosette orbit. As discussed by Born [22], this description may be extended to the n -region piecewise Coulombic field.

In summary, it is concluded that matrix elements of the Runge-Lenz vector \mathbf{A} provide a useful description of polar wave-functions such as those linear combinations of atomic orbitals known as hybrid orbitals. Specifically, the matrix elements of \mathbf{A} help establish the correspondence between wave-mechanical and classical descriptions. The properties of \mathbf{A} are described for hybrid orbitals constructed from general central-field functions for which \mathbf{A} is not diagonal in the principal quantum number n . As a consequence, these hybrid functions are characterized by greater spreads $\sigma(\mathbf{A})$ than are their hydrogenic counterparts. Analysis of the properties of a piecewise Coulombic field shows that the noncommutation of \mathbf{A} and \mathcal{H} is associated with a discontinuity in the radial derivative of the potential energy.†

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* See footnote on p. 807.

† The piecewise Coulombic example suggests a choice of P for smooth central fields not as $Ze^2\mu/\hbar$, where Ze is the true nuclear charge, but instead as $r^2(dV/dr)\mu/\hbar$, which is the choice in Eq. (27), making $[\mathbf{A}, H]=0$ within each piecewise Coulombic region. However, it is unclear whether the resulting definition of \mathbf{A} has any physical significance.

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