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Generalized Quantum Mechanical Two-Centre Problems

I. General Theory and Results for Some Two-Centre Coulomb Problems*

KLAUS HELFRICH and HERMANN HARTMANN

Institute and Centre of Theoretical Chemistry, University of Frankfurt

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Correlation diagrams for the lowest electronic states of the systems $(LiH)^{3+}$, $(HeH)^{++}$, $(LiHe)^{4+}$, H_2^+, (He, -1), and $(H, -1)^-$ (finite dipole with one electron) have been computed exactly and are discussed with special regard to the non-crossing rule and to the asymptotic behaviour of generalized diatomic orbitals.

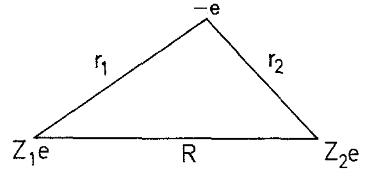
Korrelationsdiagramme für die tiefsten elektronischen Zustände der Systeme $(LiH)^{3+}$, $(HeH)^{++}$, $(LiHe)^{4+}$, H_2^+, (He, -1) und $(H, -1)^-$ (endlicher Dipol mit einem Elektron) wurden exakt berechnet und werden im Hinblick auf die Nichtüberschneidungsregel und auf das asymptotische Verhalten verallgemeinerter zweiatomiger Bahnfunktionen diskutiert.

On a calculé exactement les diagrammes de corrélation pour les plus bas états électroniques des systèmes $(LiH)^{3+}$, $(HeH)^{++}$, $(LiHe)^{4+}$, H_2^+, (He, -1) et $(H, -1)$ (dipole fini à 1 électron). La discussion porte plus spécialement sur la loi de non-intersection et sur le comportement asymptotique des orbitales diatomiques généralisées.

A. Introduction

Since the early work of Teller [1], Hylleraas [2], Jaffé [3], and Baber and Hassé [4] it has been known that the one-electron two-centre problem

$$\left(-\frac{\Delta}{2}-\frac{Z_1}{r_1}-\frac{Z_2}{r_2}\right)\chi=E\chi \tag{1}$$



is separable in prolate spheroidal coordinates

$$\begin{array}{ccc} \mu=\dfrac{r_1+r_2}{R} & \nu=\dfrac{r_1-r_2}{R} & \varphi \\ 1\leqq\mu<\infty & -1\leqq\nu\leqq 1 & 0\leqq\varphi<2\pi \end{array} \tag{2}$$

with the charges Z_1, Z_2 of distance R as foci. Later on, one-electron energies E and diatomic orbitals χ have been computed for various electronic states and for several values of R by Wallis [5] (H_2^+, HeH^{++}), Wallis, Herman, and Milnes [6] (finite dipole), Bates, Ledsham, and Stewart [7] (H_2^+), Bates and Carson [8] (HeH^{++}), Wind [9] (H_2^+), Peek [10] (H_2^+), and Hunter and Pritchard [11]. Correlation diagrams, however, which are based on exact computations and cover a large range of R, have apparently not been presented.

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On the other hand, several authors of quantum chemical textbooks have included correlation diagrams for one-electron diatomic molecules in their texts which are based nearly entirely on the non-crossing rule proved by Neumann and Wigner and on the assumption that the symmetry group of these molecules is $C_{\infty v}$ or, in the case of equal nuclei, $D_{\infty h}$. Assuming that symmetry, the energy curves of two states such as $2s\sigma_g$ and $3d\sigma_g$ of H_2^+, which transform under $D_{\infty h}$ after the same irreducible representation, are not allowed to cross. But they do cross, as exact calculations show, and therefore many correlation diagrams published are not correct.

Quite recently Coulson and Joseph [12] have shown that systems such as H_2^+ and HeH^{++} possess an additional symmetry connected with the separability of their Schrödinger equations. This symmetry gives rise to another constant of the motion, the eigenvalues of which are the possible values of the separation constant A'. For very small distances R, $-A' \approx l(l+1)$, where l is the angular momentum number of the corresponding united atom electronic state. As $2s\sigma_g(l=0)$ and $3d\sigma_g(l=2)$ belong to different eigenvalues A' of the additional constant of the motion, the crossing of their energy curves is not forbidden.

In all computational results presented here, no crossing of energy curves is observed, the states of which transform after the same irreducible representation of $C_{\infty v}(D_{\infty h})$ and simultaneously agree in the value A' of the separation constant. Crossing of terms belonging to the same irreducible representation of $C_{\infty v}(D_{\infty h})$, but differing in the corresponding values of A', occurs quite frequently.

B. Definition and Asymptotic Behaviour of Generalized Diatomic Orbitals

Generalized diatomic orbitals χ are the bound state solutions of the separable one-electron Schrödinger equation

$$\left(-\frac{\Delta}{2}-\frac{Z_1}{r_1}-\frac{Z_2}{r_2}-\frac{Q}{r_1 r_2}\right)\chi = E\chi, \tag{3}$$

in which Q is a real constant independent of the coordinates of the electron. In some applications to diatomic molecules with several electrons, generalized diatomic orbitals are to serve as a one-electron basis, Z_1, Z_2, and Q then being nonlinear variation parameters. Putting

$$\chi = \sqrt{\frac{8}{R_3}}\, U(\mu)\, V(\nu)\, \frac{e^{im\varphi}}{\sqrt{2\pi}} \qquad (m \text{ integer}), \tag{4}$$

the separated form of (3) turns out to be

$$\left[\frac{d}{d\mu}(\mu^2-1)\frac{d}{d\mu}+A'+2Q+R(Z_1+Z_2)\mu-p^2(\mu^2-1)-\frac{m^2}{\mu^2-1}\right]U(\mu)=0, \tag{5a}$$

$$\left[\frac{d}{d\nu}(1-\nu^2)\frac{d}{d\nu}-A'-R(Z_1-Z_2)\nu-p^2(1-\nu^2)-\frac{m^2}{1-\nu^2}\right]V(\nu)=0. \tag{5b}$$

Here p is the energy parameter defined by

$$p^2=-\tfrac{1}{2}\mathrm{ER}^2 \qquad (p>0) \tag{6}$$

and A' is a separation constant. Both p and A' depend on the three variables RZ_1, RZ_2, and Q; they are independent of R.

In the limiting united atom case $R \to 0$, (3) reduces to

$$\left(-\frac{\Delta}{2} - \frac{Z_1 + Z_2}{r} - \frac{Q}{r^2}\right)\psi = E\psi, \tag{7}$$

where r is the distance between the electron and the place of the two united centres with sum of charges $Z_1 + Z_2$. If

$$2Q \leqq \tfrac{1}{4} + l(l+1) \quad \text{and} \quad Z_1 + Z_2 > 0\,, \tag{8}$$

the atomic-like one-electron Schrödinger Eq. (7) possesses bound state solutions defined in spherical coordinates r, ϑ, φ and a discrete spectrum bounded from below (Kehl [18]). The solutions are

$$\psi_{nlm} = R_{nl}(r)\, p_l^{|m|}(\cos\vartheta)\, \frac{e^{im\varphi}}{\sqrt{2\pi}}\,, \tag{9}$$

where R_{nl} is described in [18] and $p_l^{|m|}$ is a normalized associated Legendre function of the first kind. (7) can be specialized to be the equation for Slater-Zener type atomic functions, and therefore generalized diatomic orbitals ($Q \neq 0$) appear to be superior to ordinary ones ($Q = 0$) as one-electron basis functions.

The one-electron energy E_{nl} corresponding to the solution (9) of (7) is

$$E_{nl} = -\frac{1}{2}\, \frac{(Z_1 + Z_2)^2}{\left[\frac{1}{2} + \sqrt{\left(\frac{1}{4} - 2Q\right) + l(l+1)} + n_r\right]^2} \tag{10}$$

where $n_r = n - l - 1$ is the number of nodes of R_{nl} [18].

A further inspection of Eqs. (5a) and (5b) shows that $U(\mu)$ tends to $R_{nl}(r)$ and $V(\nu)$ tends to $p_l^m(\cos\vartheta)$ separately for $R \to 0$. Furthermore,

$$-A' \approx l(l+1) \qquad \text{for small } R\,. \tag{11}$$

In the case of separated centres $R \to \infty$, Eq. (3) becomes approximately either

$$\left(-\frac{\Delta}{2} - \frac{Z_1}{r_1} - \frac{Z_2}{R} - \frac{Q}{r_1 R}\right)\psi = E\psi \tag{12a}$$

or

$$\left(-\frac{\Delta}{2} - \frac{Z_1}{R} - \frac{Z_2}{r_2} - \frac{Q}{R r_2}\right)\psi = E\psi\,, \tag{12b}$$

depending on whether the electron is near centre 1: $r_2 \approx R$ or near centre 2: $r_1 \approx R$.

The electronic energy is then given by

$$E_{n_1} = -\frac{\left(Z_1 + \frac{Q}{R}\right)^2}{2n_1^2} - \frac{Z_2}{R} \qquad \text{(electron near centre 1)}, \tag{13a}$$

$$E_{n_2} = -\frac{\left(Z_2 + \frac{Q}{R}\right)^2}{2n_2^2} - \frac{Z_1}{R} \qquad \text{(electron near centre 2)} \tag{13b}$$

according to Balmer's formula. $n_1(n_2)$ is the main quantum number of the solution of the hydrogenic problem (12a) ((12b)).

An exact proof of Eqs. (13) which also reveals the asymptotic form of ψ, uses relations between prolate spheroidal coordinates μ, ν, φ and parabolic coordinates ξ, η, φ. As usual, the latter ones are defined by

$$\xi = r - z \qquad \eta = r + z \qquad \varphi\,. \tag{14}$$

As a consequence,

$$\xi = \frac{R}{2}(\mu - 1)(1 - \nu) \qquad \eta = \frac{R}{2}(\mu + 1)(1 + \nu) \qquad \varphi = \varphi\,. \tag{15}$$

If we now move centre 2 to infinity ($R \to \infty$), keeping centre 1 and a point P with parabolic coordinates ξ, η, φ fixed, we obtain after some manipulation with (15)

$$\lim_{R\to\infty} \mu = 1 \qquad \lim_{R\to\infty} R(\mu - 1) = \xi \qquad \lim_{R\to\infty} R(\mu^2 - 1) = 2\xi\,, \tag{16a}$$

$$\lim_{R\to\infty} \nu = -1 \qquad \lim_{R\to\infty} R(1 + \nu) = \eta \qquad \lim_{R\to\infty} R(1 - \nu^2) = 2\eta\,. \tag{16b}$$

The asymptotic form of Eqs. (5a) and (5b) is therefore

$$\left[\frac{1}{\xi}\frac{d}{d\xi}\xi\frac{d}{d\xi} - \frac{p^2}{R^2} + \left(\frac{A' + RZ_1 + RZ_2 + 2Q}{2R}\right)\frac{1}{\xi} - \frac{m^2}{4\xi^2}\right]X(\xi) = 0\,, \tag{17a}$$

$$\left[\frac{1}{\eta}\frac{d}{d\eta}\eta\frac{d}{d\eta} - \frac{p^2}{R^2} + \left(\frac{-A' + RZ_1 - RZ_2}{2R}\right)\frac{1}{\eta} - \frac{m^2}{4\eta^2}\right]Y(\eta) = 0 \tag{17b}$$

where an expression $RZ_1 + RZ_2 + 2p^2$ was approximated by $2p^2$ and, similarly, $RZ_1 - RZ_2 + 2p^2$ was approximated by $2p^2$.

The two Eqs. (17a) and (17b) also arise when the one-electron Kepler problem is treated in a parabolic coordinate system and can be solved explicitly ([13], p. 119). Both equations are of the form

$$\left[\frac{1}{x}\frac{d}{dx}x\frac{d}{dx} - \frac{k^2}{4} + \frac{kB}{x} - \frac{m^2}{4x^2}\right]X(x) = 0 \qquad \left(\frac{k}{2} = p\right) \tag{18}$$

which possesses finite solutions

$$X(x) = e^{-\frac{kx}{2}}(kx)^{\frac{|m|}{2}} L^{|m|}_{|m|+j}(kx) \qquad \text{(with } j \text{ nodes)} \tag{19}$$

if $B = \frac{1}{2}(|m| + 1) + j$ with j a non-negative integer. This condition for B implies in connection with (17a) that

$$\frac{A' + RZ_1 + RZ_2 + 2Q}{4p} = \frac{1}{2}(|m| + 1) + S\,; \qquad S = 0, 1, 2, \ldots \tag{20a}$$

and in connection with (17b) that

$$\frac{-A' + RZ_1 - RZ_2}{4p} = \frac{1}{2}(|m| + 1) + T\,; \qquad T = 0, 1, 2, \ldots\,. \tag{20b}$$

Combining these two equations for p and A', one obtains

$$p = \frac{RZ_1 + Q}{2n_1} \text{ with } n_1 = S + T + |m| + 1\,, \tag{21}$$

$$-A' = \frac{(T-S)(RZ_1+Q)}{n_1} + (RZ_2 + Q)\,. \tag{22}$$

Eq. (21) is equivalent to Balmer's formula and slightly inferior to (13a).

This derivation shows that generalized diatomic orbitals tend to hydrogenic functions as they arise when the Kepler problem is treated in parabolic coordinates, i.e. they tend to hydrogenic functions which are, for instance, the appropriate basis for a study of the Stark effect of hydrogen. These functions possess $S + T + |m|$ nodal surfaces, S of which are paraboloids of rotation open to the right side, whereas T surfaces are paraboloids of rotation open to the left side.

In case of generalized diatomic systems with equal charges $Z_1 = Z_2 (D_{\infty h})$, the generalized diatomic orbitals tend to the normalized sum or difference of two hydrogenic Functions (S, T, m), one concentrated on each of the two centres. Here it is assumed that the midpoint of the two centres is kept fixed and the centres are moved away preserving symmetry $D_{\infty h}$.

C. Constants of the Motion

In Eq. (5a), we replace all differentiation operators $\frac{d}{d\mu}$ by corresponding partial differentiation operators $\frac{\partial}{\partial\mu}$ and multiply each side by $(1-\nu^2)\,V(\nu)$. Similarly we proceed in (5b) and multiply by $-U(\mu)\,(\mu^2-1)$. Adding the left and the right sides of the two resulting equations we obtain

$$\begin{aligned}\Bigg[&(1-\nu^2)\left(\frac{\partial}{\partial\mu}(\mu^2-1)\frac{\partial}{\partial\mu} + 2Q + R(Z_1+Z_2)\,\mu - \frac{m^2}{\mu^2-1}\right)\\ &-(\mu^2-1)\left(\frac{\partial}{\partial\nu}(1-\nu^2)\frac{\partial}{\partial\nu} - R(Z_1-Z_2)\,\nu - \frac{m^2}{1-\nu^2}\right)\\ &+A'(\mu^2-\nu^2)\Bigg]\,U(\mu)\,V(\nu) = 0\end{aligned} \tag{23}$$

or

$$A'\chi(\mu,\nu,\varphi) = A'\chi(\mu,\nu,\varphi) \tag{24a}$$

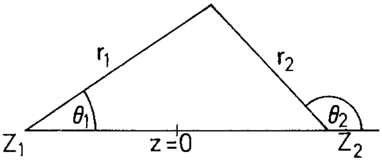
with

$$\begin{aligned}A' = \frac{-1}{\mu^2-\nu^2}\Bigg[&(1-\nu^2)\left(\frac{\partial}{\partial\mu}(\mu^2-1)\frac{\partial}{\partial\mu} + 2Q + R(Z_1+Z_2)\,\mu + \frac{\frac{\partial^2}{\partial\varphi^2}}{\mu^2-1}\right)\\ &-(\mu^2-1)\left(\frac{\partial}{\partial\nu}(1-\nu^2)\frac{\partial}{\partial\nu} - R(Z_1-Z_2)\,\nu + \frac{\frac{\partial^2}{\partial\varphi^2}}{1-\nu^2}\right)\Bigg].\end{aligned} \tag{24b}$$

The operator A' commutes with the hamiltonian $\boldsymbol{h}$ of Eq. (3) because it has the very same eigenfunctions χ which $\boldsymbol{h}$ possesses. A strict proof for commutativity may be drawn from the work of Cordes [14] on separation theory. Furthermore, A' commutes with $\frac{\hbar}{i}\frac{\partial}{\partial\varphi}$, the z-component $\boldsymbol{L}_z$ of angular momentum. Finally, A' is invariant against reflection at a plane containing the two centres 1 and 2 ($\mu'=\mu$; $\nu'=\nu$; $\varphi'=2\pi-\varphi$) and, if $Z_1=Z_2$, against inversion ($\mu'=\mu$; $\nu'=-\nu$; $\varphi'=\pi+\varphi$). So the three operators $\boldsymbol{h}$, A', and $\boldsymbol{L}_z$ form a complete set of commuting observables and provide a classification of the stationary states of the system.

A comparison with the paper of Erikson and Hill [15] (their Eq. 11) shows that

$$-A'=\Omega+Q(1-\cos(\theta_2-\theta_1)) \tag{25a}$$



where the operator Ω has the following physical significance ([15], Eq. 8)

$$\Omega=\boldsymbol{L}^2+\frac{R^2}{4}\left(\Delta-\frac{\partial^2}{\partial z^2}\right)+R(Z_1\cos\theta_1-Z_2\cos\theta_2), \tag{25b}$$

$\boldsymbol{L}^2$ is the operator of the square of angular momentum. Therefore,

$$-A'=\boldsymbol{L}^2+\frac{R^2}{4}\left(\Delta-\frac{\partial^2}{\partial z^2}\right)+R(Z_1\cos\theta_1-Z_2\cos\theta_2)+Q(1-\cos(\theta_2-\theta_1)) \tag{26}$$

all parts of which vanish in the limit $R=0$ except $\boldsymbol{L}^2$.

D. Virial Theorem

First, three operators are defined by

$$\boldsymbol{t}_2=-R^2\frac{\Delta}{2}; \quad \boldsymbol{v}_1=-R\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}\right); \quad \boldsymbol{v}_2=-\frac{R^2Q}{r_1r_2}. \tag{27}$$

They are evidently independent of R when expressed in spheroidal coordinates. According to Eq. (3), the hamiltonian $\boldsymbol{h}$ is

$$\boldsymbol{h}=\boldsymbol{T}+\boldsymbol{V}_1+\boldsymbol{V}_2 \tag{28}$$

with

$$\boldsymbol{T}=\frac{1}{R^2}\boldsymbol{t}_2; \quad \boldsymbol{V}_1=\frac{1}{R}\boldsymbol{v}_1; \quad \boldsymbol{V}_2=\frac{1}{R^2}\boldsymbol{v}_2 \tag{29}$$

so that

$$\begin{aligned}\left.\frac{\partial\boldsymbol{h}}{\partial R}\right|_{Z_1,Z_2,Q}&=-\frac{2}{R^3}\boldsymbol{t}_2-\frac{1}{R^2}\boldsymbol{v}_1-\frac{2}{R^3}\boldsymbol{v}_2\\&=\frac{1}{R}(-2\boldsymbol{T}-\boldsymbol{V}_1-2\boldsymbol{V}_2).\end{aligned} \tag{30}$$

Assuming χ to be an eigenfunction of the hamiltonian (28) with eigenvalue E, we obtain E as the expectation value of $\boldsymbol{h}$ computed with χ:

$$E=(\chi|\boldsymbol{h}|\chi)\,. \tag{31}$$

From the Hellman-Feynman-theorem (see, for instance, [16])

$$\frac{\partial E}{\partial\lambda}=\left(\chi\left|\frac{\partial\boldsymbol{h}}{\partial\lambda}\right|\chi\right) \tag{32}$$

and from (30) we conclude that

$$\frac{\partial E}{\partial R}_{Z_1,Z_2,Q}=\left(\chi\left|\frac{1}{R}(-2\boldsymbol{T}-V_1-2V_2)\right|\chi\right) \tag{33}$$

or

$$R\frac{\partial E}{\partial R}\bigg|_{Z_1,Z_2,Q}=-2\bar{\boldsymbol{T}}-\bar{V}_1-2\bar{V}_2\,. \tag{34}$$

The right hand side of this equation differs from that encountered in the usual description of the virial theorem for diatomic molecules by the term $-2\bar{V}_2=-2Q\left(\chi\left|\frac{1}{r_1r_2}\right|\chi\right)$. By the way,

$$\left(\chi\left|\frac{1}{r_1r_2}\right|\chi\right)=\frac{4}{R^2}\int_1^\infty U^2(\mu)\,\mathrm{d}\mu\cdot\int_{-1}^{1}V^2(\nu)\,\mathrm{d}\nu\,. \tag{35}$$

E. Method of Computing p and A'

The method of computation that has been used here is very similar to that which was earlier applied to homonuclear diatomic molecules ($Z_1=Z_2$; $Q=0$) and was described in [17] (Appendix 1). For $U(\mu)$, the solution of (5a), a linear expansion in terms of associated Laguerre polynomials is assumed:

$$U(\mu)=e^{-\frac{x}{2}}(\mu^2-1)^{\frac{|m|}{2}}\sum_{j=0}^{\infty}c_jL_{|m|+j}^{|m|}(x)\qquad\text{with } x=2p(\mu-1)\,. \tag{35a}$$

The resulting three-term recursion formula for the components of $\boldsymbol{c}$ is:

$$\alpha_jc_{j-1}+(\beta_j+A')\,c_j+\gamma_jc_{j+1}=0 \tag{36}$$

with

$$\alpha_j=(j+|m|+1)\,(j-|m|-\sigma)\,,$$

$$\beta_j=2Q+(|m|+1)\,(|m|+\sigma)+2p\sigma-2j(j+2p-\sigma)\,,$$

$$\gamma_j=j(j-1-\sigma)\,,$$

$$\sigma=\frac{RZ_1+RZ_2}{2p}-|m|-1\,.$$

For $V(\nu)$, the solution of (5b), we assume

$$V(\nu)=e^{p\nu}\sum_{k=0}^{\infty}d_kP_{|m|+k}^{|m|}(\nu)\,. \tag{37}$$

The resulting three-term recursion formula for the components of $\boldsymbol{d}$ is the very same as in the case of one-electron diatomic molecules ($Q=0$) and is given in [13] (page 130).

The three-term recursion formulas are, in matrix form,

$$\boldsymbol{A}\boldsymbol{c}=\lambda\boldsymbol{c}\,, \qquad \boldsymbol{B}\boldsymbol{d}=\lambda\boldsymbol{d}\,, \tag{38}$$

where $\boldsymbol{A}$ and $\boldsymbol{B}$ are tridiagonal matrices depending on the energy parameter p_1 and $-\lambda=A'$ is the separation constant.

These coupled two eigenvalue equations are solved simultaneously for p and λ by applying the Newton-Raphson-algorithm for two unknowns (p and λ) to the system of two secular equations

$$\begin{aligned} F(p,\lambda) &\equiv \det(\boldsymbol{A}(p)-\lambda\underset{\sim}{1})=0\,, \\ G(p,\lambda) &\equiv \det(\boldsymbol{B}(p)-\lambda 1)=0 \end{aligned} \tag{39}$$

following from (38). Recursion formulas for the evaluation of the two determinants F and G and for their four partial derivatives $\frac{\partial F}{\partial p}, \frac{\partial F}{\partial \lambda}, \frac{\partial G}{\partial p}, \frac{\partial G}{\partial \lambda}$, which are needed for the NR-algorithm, have been given in [17]. Initial approximations for p and λ necessary for this algorithm are obtained from (10) and (11), for small values of R. In the later stages of computation, quadratic extrapolation for the initial approximatio is applied when raising the value of R. This holds for systems having bound electronic states in the limit $R\to 0$. If there is no united centre system with bound states as in the case of the finite dipole, initial approximations for p and λ are obtained from (21) and (22), and the computing process is performed by stepping down from high values of R to lower ones.

These procedures give p, A' (and of course the one-electron energy E) as functions of R over a wide range of R; within each single computation we assume Z_1, Z_2, Q and the three quantum numbers n, l, m (S, T, m) to be constants.

F. Results for Two-Centre Coulomb Problems

In each of the figures which will be discussed now it is assumed that

a) $Q=0$, b) $Z_1 \geqq Z_2$ (without loss of generality), c) $Z_1 : Z_2 = \text{const.}$

Each of the following diagrams holds for all one-electron systems (1) which fulfil conditions b) and c) due to the following choice of variables: E/Z_2^2 is plotted against RZ_2. Because the energy parameter p depends on RZ_2 only, the ratio $Z_1 : Z_2$ being prescribed, the quantity

$$E/Z_2^2 = -\frac{2p^2}{(RZ_2)^2}$$

is a function of RZ_2 alone, independent of R.

In order to separate the different energy curves in the diagrams better, a fictive quantum number n_0 is defined by

$$n_0=\sqrt{\frac{E^0(1s)}{E}} \quad \text{with} \quad E^0(1s)=-\frac{(Z_1+Z_2)^2}{2}=-\frac{Z_2^2}{2}\left(1+\frac{Z_1}{Z_2}\right)^2 . \tag{40}$$

Actually, it is this quantity n_0 that was plotted against RZ_2.

The separated atom designation S, T, m of the states treated and the centre to which it refers was found by use of the asymptotic formulas (13a) and (22) and is in agreement with the rules.

a) $S=n_0-l-1$, b) $m=m$

and a more complicated rule for T given by Monroe [19] and by Marrack [20].

a) $Z_1:Z_2=3$, Fig. 1.

$(\mathrm{LiH})^{3+}$ belongs to this class of problems. States plotted in Table 1.

Here, energies of states $3p\sigma$ and $3d\sigma$ cross at about $RZ_2=1a_0$ $E(4f\sigma)$ and $E(3s\sigma)$ cross at about $4a_0$ and $E(4f\sigma)$ and $E(3p\sigma)$ do so at about $5a_0$.

If $E+\frac{Z_1Z_2}{R}$ is plotted against R for $(\mathrm{LiH})^{3+}$, a shallow minimum is found near $R=6a_0$ for $3d\sigma$.

b) $Z_1:Z_2=2$, Fig. 2.

$(\mathrm{HeH})^{++}$ belongs to this class of problems. The computations cover a wider range of R and one state $4f\sigma$ more than those performed by Bates and Carson [8]. States plotted in Table 2.

$E(2s\sigma)$ and $E(3d\sigma)$ cross at about $RZ_2=4\,a_0$. $E(3p\sigma)$ and $E(3d\sigma)$ cross at about $6\,a_0$. Finally, $E(4f\sigma)$ and $E(3s\sigma)$ cross at about $4\,a_0$ and $E(4f\sigma)$ and $E(3p\sigma)$ do so at about $6\,a_0$. $E(2p\sigma)+(Z_1Z_2)/R$ has, for $(\mathrm{HeH})^{++}$, a shallow minimum near $4\,a_0$, which has already been known [8].

c) $Z_1:Z_2=3:2$, Fig. 3.

$(\mathrm{LiHe})^{4+}$ belongs to this class of problems. States plotted in Table 3.

$E(2s\sigma)$ and $E(3d\sigma)$ cross at about $RZ_2=3.5\,a_0$. Besides, $E(3p\sigma)$ and $E(3d\sigma)$ cross at about $RZ_2=2\,a_0$. Further cross points are:

$$(3s\sigma,4d\sigma)\quad(3s\sigma,4f\sigma)\quad(3s\sigma,5g\sigma)\quad(3p\sigma,4f\sigma)\quad(3p\sigma,5g\sigma)$$
$$(4d\sigma,4f\sigma)\quad(4d\sigma,5g\sigma)\quad(3p\pi,4f\pi).$$

d) $Z_1:Z_2=1$.

H_2^+ belongs to this class of problems. The corresponding energy diagram has been given in [17]. States plotted are those with $n_0\leqq 3$ and $4f\sigma_u$. The relation between united-atom quantum numbers n_0, l and separated-atoms quantum numbers S, T is:

$$S=n_0-l-1$$
$$T=\left[\frac{l-|m|}{2}\right] \qquad ([x]=\mathrm{entier}(x)).$$

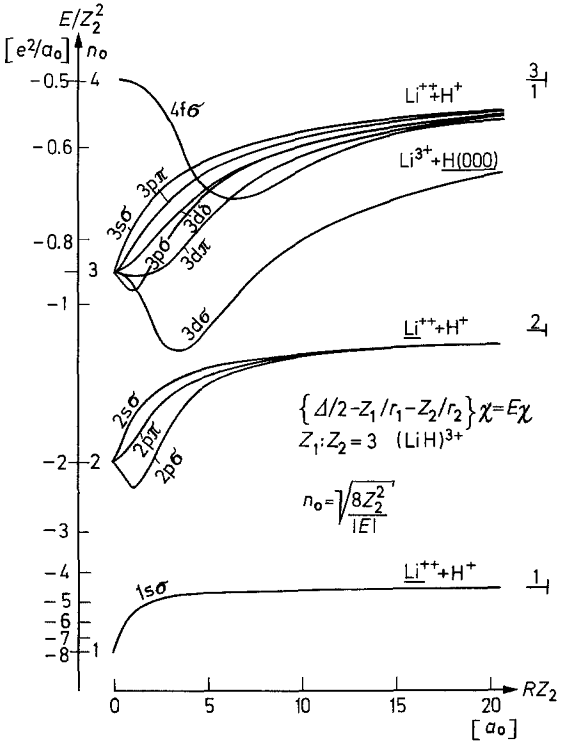


Fig. 1

Table 1

United atom-designation	Separated atoms-designation					
$n_0 l \lvert m \rvert$	centre	S	T	$\lvert m \rvert$	n_∞ [a]	
1sσ	1 (Li)	0	0	0	1	(Li⁺⁺ + H⁺)
2sσ		1	0	0	2	
2pσ		0	1	0		
2pπ		0	0	1		
3sσ		2	0	0	3	
3pσ		1	1	0		
4fσ		0	2	0		
3pπ		1	0	1		
3dπ		0	1	1		
3dδ		0	0	2		
3dσ	2 (H)	0	0	0	1	(Li⁺⁺⁺ + H)

[a] $n_\infty = \begin{cases} n_1 & \text{if the electron is near centre 1.} \\ n_2 & \text{if the electron is near centre 2.} \end{cases}$

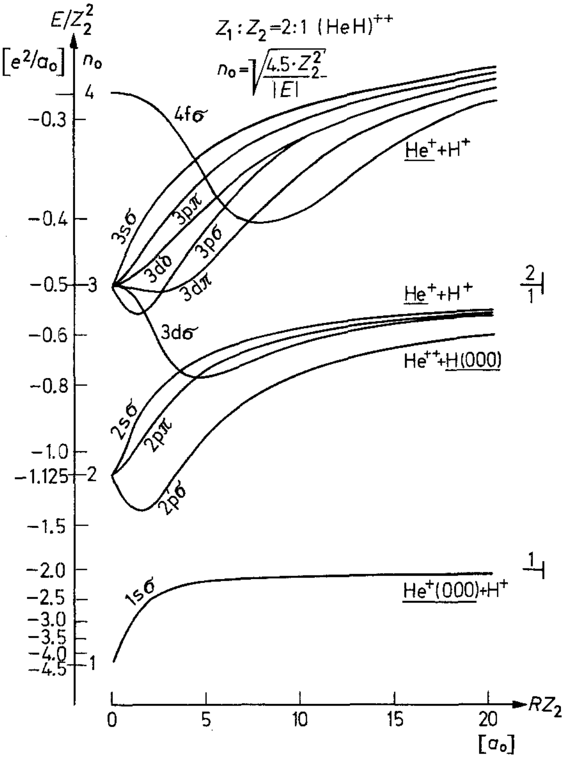


Fig. 2

Table 2

United atom-designation	Separated atoms-designation					
$n_0 l \lvert m \rvert$	centre	S	T	$\lvert m \rvert$	n_∞	
1sσ	1 (He)	0	0	0	1	(He$^+$ + H$^+$)
2sσ		1	0	0	2	
3dσ		0	1	0		
2pπ		0	0	1		
3sσ		2	0	0	3	
3pσ		1	1	0		
4fσ		0	2	0		
3pπ		1	0	1		
3dπ		0	1	1		
3dδ		0	0	2		
2pσ	2 (H)	0	0	0	1	(He^{++} + H)

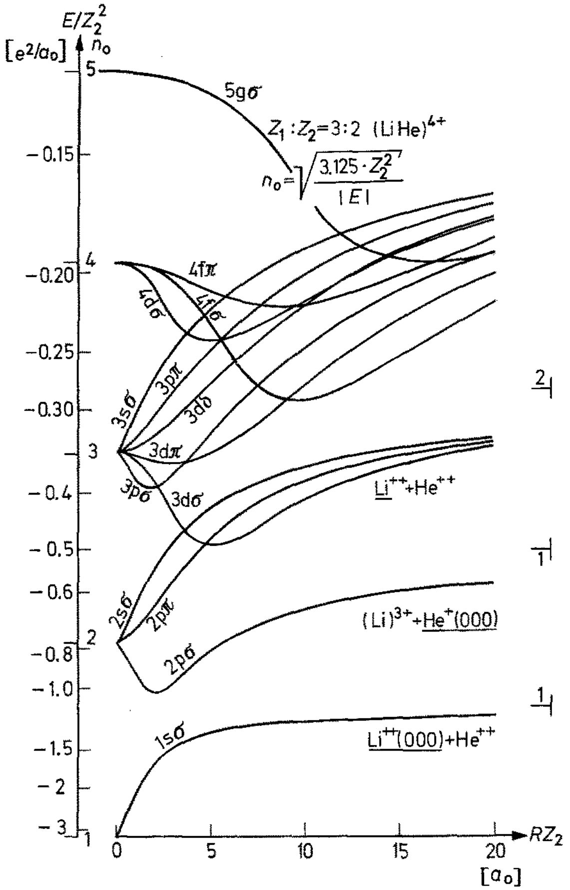


Fig. 3

Table 3

United atom-designation	Separated atoms-designation					
$n_0 l\vert m\vert$	centre	S	T	$\vert m\vert$	n_∞	
1sσ	1 (Li)	0	0	0	1	($\mathrm{Li}^{++}+\mathrm{He}^{++}$)
2sσ		1	0	0	2	
3dσ		0	1	0		
2pπ		0	0	1		
3sσ		2	0	0	3	
4dσ		1	1	0		
5gσ		0	2	0		
3pπ		1	0	1		
4fπ		0	1	1		
3dδ		0	0	2		
2pσ	2 (He)	0	0	0	1	($\mathrm{Li}^{+++}+\mathrm{He}^{+}$)
3pσ		1	0	0	2	
4fσ		0	1	0		
3dπ		0	0	1		

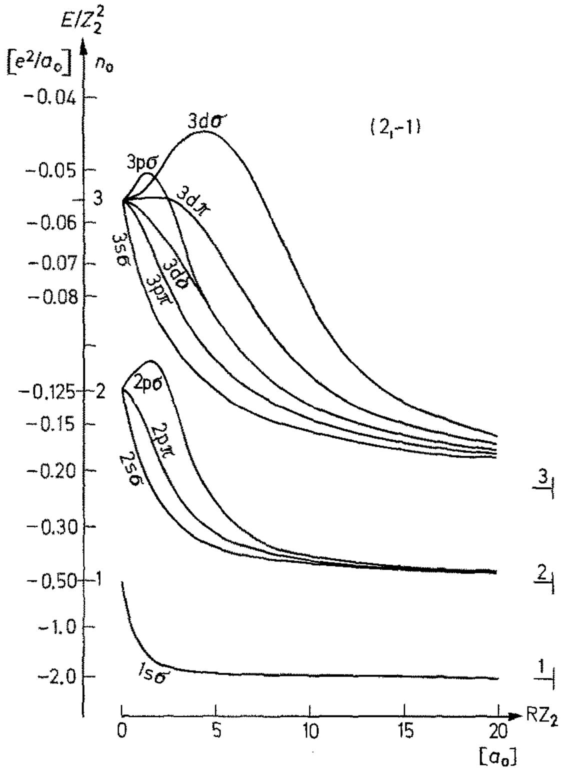


Fig. 4

Table 4

United atom-designation	Separated atoms-designation				
$n_0 l \lvert m \rvert$	centre 1 S	T	$\lvert m \rvert$	n_1	$(He^+ + (-1))$
1sσ	0	0	0	1	
2sσ	1	0	0	2	
2pσ	0	1	0		
2pπ	0	0	1		
3sσ	2	0	0	3	
3pσ	1	1	0		
3dσ	0	2	0		
3pπ	1	0	1		
3dπ	0	1	1		
3dδ	0	0	2		

Beside of the cross point between $E(2s\sigma_g)$ and $E(3d\sigma_g)$ at $4\,a_0$ mentioned in the introduction, a further cross point occurs between $E(3p\sigma_u)$ and $E(4f\sigma_u)$ at about $RZ = 12\,a_0$.

e) The case $Z_1 : Z_2 = 0 : 1$ (H) is trivial and is only mentioned for the sake of completeness. Energy curves are parallels to the RZ_2-axis. $n_0 = n_2$ gives $T = l - m$; besides $S = n_0 - l - 1$. The process of enlargening RZ_2 is only a mathematical procedure equivalent to a steady change of transformation of the original basis $\{|n_0 l\, m)\}$ until the final basis is $\{|S\, T\, m)\}$.

f) $Z_1 : Z_2 = 2 : (-1)$, Fig. 4.

Here we find He$^+$, disturbed by one negative charge. States plotted in Table 4.

As $n_1 = n_0$, $T = l - |m|$ just as in the previous case of hydrogen ($Z_1 : Z_2 = 0 : 1$). $E(3p\sigma)$ and $E(3d\sigma)$ cross near $-RZ_2 = 2\,a_0$.

g) $Z_1 : Z_2 = 1 : (-1)$.

One electron in the field of a finite dipole is representative for a class of problems for which no united atom problem with bound states exists. So it is natural to classify the states after the separated atom case and label them with S, T, m.

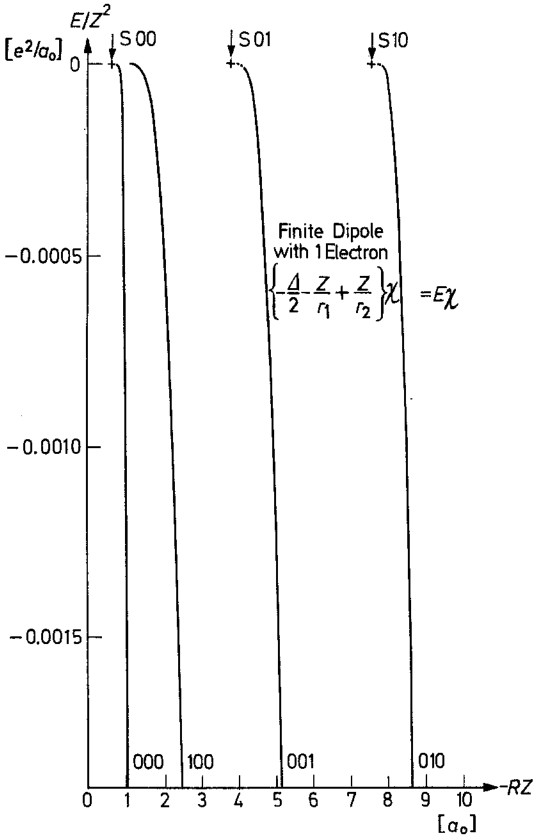


Fig. 5

Former calculations of Wallis *et al.* [6] have been extended to include states with $n_1 = 4$ and to approach nearer to the zero energy limit with RZ_2 (Fig. 5).

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Dr. K. Helfrich
Prof. Dr. H. Hartmann
Institut und Zentrum für Theoretische Chemie
der Universität
6000 Frankfurt am Main 1, Robert-Mayer-Str. 11