

# Generalized Quantum Mechanical Two-Centre Problems

## II. The Case of Equal Centres

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For the one-electron Schrödinger equation among the solutions of which the Slater-Zener-type functions can be found, it is shown, that it can be generalized to the two-centre case only in one way, if one demands separability in prolate spheroidal coordinates, and if in addition to the Coulomb term of the potential energy there shall be an additional function of the product  $r_1 \cdot r_2$  only. The generalized problem with a potential energy of the form  $V(r) = -Z_1/r_1 - Z_2/r_2 - Q(R)/r_1 r_2$  is studied for the case of two equal centres  $Z_1 = Z_2 = Z \geq 0$  with regard to the existence and number of bound states. The results are extended as far as possible also to the case with unequal centres. For some examples with equal centres wave functions and correlation diagrams have been computed exactly for the lowest electronic states.

Es wird gezeigt, daß sich die Ein-Elektron-Schrödingergleichung, unter deren Lösungen die Slater-Zener-Funktionen sind, nur auf eine Art auf den Zwei-Zentren-Fall verallgemeinern läßt, wenn Separierbarkeit in elliptischen Koordinaten verlangt wird, und wenn zusätzlich zum Coulomb-Anteil der potentiellen Energie ein Zusatzglied, das nur eine Funktion des Produkts  $r_1 \cdot r_2$  ist, vorhanden sein soll. Das verallgemeinerte Problem mit der potentiellen Energie der Form  $V(r) = -Z_1/r_1 - Z_2/r_2 - Q(R)/r_1 r_2$  wird im Hinblick auf die Existenz und Anzahl gebundener Zustände für den Fall gleicher Zentren  $Z_1 = Z_2 = Z \geq 0$  untersucht. Die Ergebnisse werden soweit möglich auf den Fall ungleicher Zentren erweitert. Für einige Beispiele mit gleichen Zentren wurden Wellenfunktionen und Korrelationsdiagramme für die tiefsten elektronischen Zustände exakt berechnet.

L'équation de Schrödinger mono-électronique qui comporte parmi ses solutions des fonctions du type Slater-Zener, ne peut être généralisée au cas à deux centres que d'une seule manière en exigeant la séparabilité en coordonnées sphéroïdales allongées et en ajoutant au terme coulombien d'énergie potentielle une fonction du produit  $r_1 r_2$  seulement. Le problème généralisé avec une énergie potentielle de la forme

$$V(r) = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{Q(R)}{r_1 r_2}$$

est étudié pour le cas de deux centres identiques  $Z_1 = Z_2 = Z \geq 0$ , en ce qui concerne l'existence et le nombre d'états liés. Les résultats sont étendus autant que possible au cas avec centres différents. Pour certains exemples à centres identiques on a calculé exactement les fonctions d'ondes et les diagrammes de corrélation pour les états électroniques les plus bas.

### 1. Introduction

In Part I [1] it has been proposed to study the separable one-electron Schrödinger equation:

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

The bound state solutions of this equation, the generalized diatomic orbitals, are to serve as a one-electron basis in applications to diatomic molecules<sup>1</sup>. Functions of this kind represent a generalization of the Slater-Zener-type atomic functions, since the eigenvalue equation for the "united centre" case  $R \rightarrow 0$ :

$$\left(-\frac{A}{2} - \frac{Z_1 + Z_2}{r} - \frac{Q_0}{r^2}\right)\chi = E\chi \quad (2)$$

(with the limiting value  $Q_0 \neq 0$  of  $Q(R)$  for  $R \rightarrow 0$ ) can be specialized to become an equation, among the solutions of which the Slater-Zener-type atomic functions can be found.

From the literature it is well known that, for certain parameter values  $Z_1, Z_2$  or  $Q$  in Eq. (1) and (2), the spectrum and the eigenfunctions behave rather extraordinary in comparison with some standard problems in quantum mechanics e.g. the H atom or the  $H_2^+$  molecule ion. For example no bound states exist in the case of  $Z_1 = -Z_2, Q = 0$  (finite dipole) in Eq. (1) if the dipole moment is below a certain limit (cf. e.g. [2]). For the one-centre problem (2) with  $(Z_1 + Z_2) = 0$  it is known, that for certain values of  $Q_0 > 0$  the spectrum is not bounded from below while for other values of  $Q_0 > 0$  no discrete eigenvalues exist (cf. e.g. [3, 4]). These special cases demand a careful examination of the differential Eqs. (1) and (2) before a calculation of the eigenvalues and eigenfunctions and before an application to molecular problems. In this paper the two-centre cases with equal centres  $Z_1 = Z_2 = Z \geq 0$  will be studied. The results however will be extended as far as possible also to cases with different centres. In all cases  $Q$  does not depend on the electronic coordinates, however it can be a function of the distance  $R$  of the two centres. The results for the united-centre case (2) can be found in the literature or may be derived easily for some special cases [5, 1], and will be only reported here together with the results for the two-centre case and the case  $R \rightarrow \infty$  [1] in Table 1 below.

## 2. Extension of Slater-Zener-Type Functions to the Two-Centre Case

The potentials of the class of separable problems with cylinder symmetry are of the general form:

$$V(r) = \frac{X(\mu) + Y(\nu)}{\mu^2 - \nu^2} \quad \begin{array}{l} (X \text{ and } Y \text{ arbitrary functions}) \\ \mu = (r_1 + r_2)/R, \nu = (r_1 - r_2)/R \end{array} \quad (3)$$

For gaining a set of two-centre functions which represent a generalization of Slater-Zener-type functions it is not possible, as it might seem for a moment, to start from a one-electron Schrödinger equation:

$$\left(-\frac{A}{2} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{Q_1}{r_1^2} - \frac{Q_2}{r_2^2}\right)\lambda = E\lambda. \quad (4)$$

<sup>1</sup> Potentials of this kind with an additional term  $V_T(r) = (a\mu^2 + b\nu^2)/r_1 r_2$  have been proposed as model potentials in one-electron theories for many-electron molecules [18, 19]. These potentials will not be treated here, since there are enough non-linear variational parameters contained in the present basis which shall be used e.g. in CI calculations. However one may show easily that the results about the discrete spectrum in Chapter c) below are not affected at all by an additional term  $[a(\mu^2 - 1) + a]/r_1 r_2$ .  $V_T$  may be reduced to this form without loss of generality [19].

This problem has no potential of the separable form (3). The whole class of separable problems with potentials which can be written as a sum of two terms which are functions of  $r_1$  and  $r_2$  respectively:

$$V_S(r) = g_1(r_1) + g_2(r_2) \quad (g_1 \text{ and } g_2 \text{ arbitrary functions}) \quad (5)$$

has been given by Coulson and Joseph [6], and consists essentially of such potentials which are a sum of Coulomb terms.

If one goes over to the limit  $R \rightarrow 0$  in the way described in [1], the potential energy of Eq. (3) tends to:

$$V(R=0) = \lim_{R \rightarrow 0} \frac{R^2 X(2r/R)}{4r^2}$$

under the assumption that  $Y(v)$  depends on the parameter  $R$  in such a way that it will vanish in the limit case so that  $V(R=0)$  will be a pure radial potential. If one demands that  $V(R=0)$  should be of the form:

$$V(R=0) = -\frac{Z_1 + Z_2}{r} - \frac{Q_0}{r^2}$$

the form of  $X(\mu)$  is no longer arbitrary, while  $Y(v)$  can still be chosen in an arbitrary way in the corresponding two-centre case. An especially simple form of  $V(r)$  is then

$$V(r) = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{Q}{r_1 r_2}$$

apart from the arbitrary  $Y(v)$ -part. However this potential is the only case of a potential with cylinder symmetry of the general form:

$$V_P(r) = \frac{Z_1}{r_1} - \frac{Z_2}{r_2} + g(r_1 \cdot r_2) \quad (6)$$

for which the one-electron Schrödinger equation is separable in prolate spheroidal coordinates. This can be proved in the following way: separability is given if and only if for all values of  $r_1$  and  $r_2$  Eq. (3) holds for the potential  $V(r)$ . Using Eq. (6), Eq. (3) can be written as:

$$\frac{-Z_1 r_2 - Z_2 r_1 + r_1 \cdot r_2 \cdot g(r_1 \cdot r_2)}{r_1 \cdot r_2} = \frac{X(\mu) + Y(v)}{r_1 \cdot r_2}$$

Since the terms with  $Z_1$  and  $Z_2$  can be written as a sum of a function of  $\mu$  and a function of  $v$  respectively one has:

$$p \cdot g(p) = \tilde{X}(\mu) + \tilde{Y}(v) \quad (7)$$

with

$$p = r_1 \cdot r_2; \quad (\mu = r_1 + r_2; \quad v = r_1 - r_2; \quad R = 1).$$

By differentiation of Eq. (7) after  $r_1$  one gets:

$$r_2 g(p) + p \frac{dg(p)}{dp} r_2 = \frac{d\tilde{X}(\mu)}{d\mu} + \frac{d\tilde{Y}(v)}{dv} \quad (8a)$$

and by differentiation of Eq. (7) after  $r_2$ :

$$r_1 g(p) + p \frac{dg(p)}{dp} r_1 = \frac{d\tilde{X}(\mu)}{d\mu} - \frac{d\tilde{Y}(v)}{dv}. \quad (8b)$$

Addition of (8a) and (8b) and subtraction of (8a) and (8b) respectively yields:

$$g(p) + p \frac{dg(p)}{dp} = \frac{2}{\mu} \frac{d\tilde{X}(\mu)}{d\mu}, \quad (9a)$$

$$g(p) + p \frac{dg(p)}{dp} = -\frac{2}{v} \frac{d\tilde{Y}(v)}{dv} \quad (9b)$$

From these equations it follows:

$$\frac{2}{\mu} \frac{d\tilde{X}(\mu)}{d\mu} = -\frac{2}{v} \frac{d\tilde{Y}(v)}{dv}. \quad (10)$$

Eq. (10) is true for all values of  $\mu$  and  $v$  only if both sides of it are constants  $C'$ :

$$\frac{2}{\mu} \frac{d\tilde{X}(\mu)}{d\mu} = C', \quad (11a)$$

$$-\frac{2}{v} \frac{d\tilde{Y}(v)}{dv} = C'. \quad (11b)$$

Integration leads to:

$$\tilde{X}(\mu) = C\mu^2 + D_1, \quad (12a)$$

$$\tilde{Y}(v) = -Cv^2 + D_2. \quad (12b)$$

If these functions are introduced into Eq. (7) one obtains the function  $g$ :

$$g(p) = \frac{D_1 + D_2}{\mu^2 - v^2} + C, \quad (13)$$

$$g(r_1 \cdot r_2) = \frac{D}{r_1 r_2} + C. \quad (14)$$

Therefore the function:

$$g(r_1 \cdot r_2) = \frac{Q(R)}{r_1 r_2} \quad (15)$$

leads, up to an additive constant, to the only potential of the general form (6) for which the Schrödinger equation is separable in prolate spheroidal coordinates. (The occurring functions are supposed to be differentiable.) The lines of constant potential of the additional potential (15) alone are given by lemniscates.

### 3. The Discrete Spectrum of the Two-Centre Problem

The following theorem about the existence and number of bound state solutions of the Schrödinger Eq. (1) shall be proved:

*Theorem. a) If  $R(Z_1 + Z_2) > 0$ , Eq. (1) has (independent of the value of  $Q$ ) infinitely many discrete eigenvalues bounded from below.*

b) If  $Z_1 = Z_2 = 0$  and  $2Q - l(l+1) \leq 1/4$  then there are no discrete eigenvalues.  
 For  $Z_1 = Z_2 = 0$  and  $2Q - l(l+1) > 1/4$  there are infinitely many eigenvalues of Eq. (1) bounded from below.

c) If  $R(Z_1 + Z_2) \leq 0$  (and  $Q \geq 0$ ) and if

$$R(Z_1 + Z_2) + 2Q + A'_{v0} \leq 1/4$$

there are no eigenvalues of Eq. (1).

If  $R(Z_1 + Z_2) \leq 0$  (and  $Q \geq 0$ ) and if

$$R(Z_1 + Z_2) + 2Q + A'_{v0} > 1/4$$

there are at most a finite number of eigenvalues of Eq. (1).

$A'_{v0}$  is the greatest value on one  $A'_v(p^2)$ -curve in the range  $p^2 \geq 0$  (see below). Those values of the separation constants, for which there are eigenvalues of Eq. (1), may be determined numerically (see Section c) below).

d) If  $Z_1 \leq 0$ ,  $Z_2 \leq 0$  and simultaneously  $Q \leq 0$ , no bound states exist since there are no attracting centres (trivial case).

*Proof.* The first results about the discrete spectrum of the partial differential operator of Eq. (1) can be obtained at once with the general theorems of Kato [7, 8]. The formal differential operator of Eq. (1) determines uniquely a self-adjoint operator with a certain domain in the Hilbert space of square integrable functions over the three-dimensional Euclidian space. This follows from the fact that the potential energy is locally square integrable and that it remains bounded for  $|r| \rightarrow \infty$  for it has no stronger singularity in any space point than the potential  $1/r$ .

From the same reasons it follows that the spectrum of the operator of Eq. (1) is bounded from below. The continuous spectrum covers the nonnegative real axis, since  $V(r) \rightarrow 0$  for  $|r| \rightarrow \infty$ . The spectrum on the negative real axis contains (if any) only isolated eigenvalues of finite multiplicity. It is clear that the Schrödinger Eq. (1) has no negative energy eigenvalues, if there are no attractive centres, that means if  $Z_1 \leq 0$ ,  $Z_2 \leq 0$  and simultaneously  $Q \leq 0$  (case d)). So furtheron only those cases have to be examined with regard to bound states for which there is at least one attractive centre.

Further results about the spectrum may be obtained from the separable partial differential equation in prolate spheroidal coordinates which is derived from (1). With the product function:

$$\chi = P(\mu, \nu) \frac{e^{im\phi}}{\sqrt{2\pi}} \quad (m \text{ integer}) \quad (16)$$

one obtains:

$$\frac{1}{\mu^2 - \nu^2} \left\{ -\frac{\partial}{\partial \mu} (\mu^2 - 1) \frac{\partial}{\partial \mu} - \frac{\partial}{\partial \nu} (1 - \nu^2) \frac{\partial}{\partial \nu} + \left( \frac{m^2}{\mu^2 - 1} - R(Z_1 + Z_2)\mu + R(Z_1 - Z_2)\nu - 2Q(R) + \frac{m^2}{1 - \nu^2} \right) \right\} \quad (17)$$

$$\cdot P(\mu, \nu) = -p^2 P(\mu, \nu)$$

$$\text{with } p^2 = -1/2 ER^2 \quad (p > 0).$$

It is now possible to apply the separation theory of Cordes [9] to the selfadjoint operator of Eq. (17) [5]. According to the theory of Cordes the eigenvalues of Eq. (17) are those values  $-p^2$  and only those for which there exists at least one value of  $A'$ , so that the equations:

$$\left\{ \frac{d}{d\mu} (\mu^2 - 1) \frac{d}{d\mu} - p^2 (\mu^2 - 1) + R(Z_1 + Z_2)\mu + 2Q + A' - \frac{m^2}{\mu^2 - 1} \right\} U(\mu) = 0, \quad (18)$$

$$\left\{ \frac{d}{dv} (1 - v^2) \frac{d}{dv} - p^2 (1 - v^2) - R(Z_1 - Z_2)v - A' - \frac{m^2}{1 - v^2} \right\} V(v) = 0 \quad (19)$$

simultaneously have solutions which have to fulfil certain requirements of square integrability and of eventual additional boundary conditions [5].

Those parameter pairs  $(p^2, A'_v)$  of the  $v$ -Eq. (19) for which there are solutions which satisfy the boundary conditions are represented by a set of curves in the real  $(p^2, A')$ -plane. For the derivative  $dA'_v/d(p^2)$  of all the functions  $A'_v(p^2)$  it can be shown [9] that:

$$-1 < \frac{dA'_v}{d(p^2)} < 0 \quad (0 \leq p^2 < +\infty). \quad (20)$$

A survey over the solutions of the  $\mu$ -Eq. (18) and the corresponding parameter pairs  $(p^2, A'_\mu)$  can be obtained with the following eigenvalue problem ([9], II, p. 383):

$$\frac{1}{(\mu^2 - 1) \cos \theta + \sin \theta} \cdot \left\{ -\frac{d}{d\mu} (\mu^2 - 1) \frac{d}{d\mu} + \left( \frac{m^2}{\mu^2 - 1} - R(Z_1 + Z_2)\mu - 2Q + p_0^2 (\mu^2 - 1) - A_0 \right) \right\} \quad (21)$$

$$\cdot f = \alpha f, \quad 0 < \theta < \frac{\pi}{2}.$$

If the problem has eigenvalues  $\alpha$  and eigenfunctions  $f$  then the  $\mu$ -Eq. (18) possesses the required solutions  $U(\mu)$  belonging to the parameter pairs  $(p_0^2 - \alpha \cos \theta, A_0 + \alpha \sin \theta)$ . For a further simplification one can choose  $\theta = \pi/4$  and therefore  $\cos \theta = \sin \theta$ . According to Friedrichs [10] one obtains the deepest point  $\alpha_0$  of the non-discrete part of the spectrum of the operator of Eq. (21):

$$\alpha_0 = \frac{p_0^2}{\cos \theta}. \quad (22)$$

The existence and the number of discrete eigenvalues of Eq. (21) may be recognized from the number of zeros of the solutions of the corresponding differential equation for the deepest point  $\alpha_0$  of the non-discrete spectrum:

$$\left\{ \frac{d}{d\mu} (\mu^2 - 1) \frac{d}{d\mu} + \left( -\frac{m^2}{\mu^2 - 1} + R(Z_1 + Z_2)\mu + (2Q + A_0 + p_0^2) \right) \right\} f = 0. \quad (23)$$

The proof can be completed in the following way now: the position of the parameter pairs  $(p^2, A'_\mu)$  relative to the straight line  $A' = (1/4 - 2Q) - p^2$  in the  $(p^2, A')$ -plane is decisive for the existence of acceptable solutions of the  $\mu$ -Eq. (18), as will be shown below. On the other hand the position of the curves  $A'_v(p^2)$  (for which there are

solutions of the  $\nu$ -Eq. (19) relative to this line can be recognized from the value  $A'_\nu(p^2=0)$  and the range of possible values of the gradient (20) of  $A'_\nu(p^2)$ . Those regions of parameter values  $(p^2, A')$  for which both Eqs. (18) and (19) have solutions, can then be determined from the relative position of the regions of acceptable parameter values  $A'_\mu(p^2)$  and  $A'_\nu(p^2)$ .

a) Case with  $R(Z_1 + Z_2) > 0$

If  $R(Z_1 + Z_2) > 0$  the solutions of the differential Eq. (23) always have (independent of the values of  $Q$ ,  $A'_0$  and  $p_0^2$ ) infinitely many zeros (according to a theorem of Kneser [11]). Therefore there is an infinite number of discrete eigenvalues  $\alpha$  below  $\alpha_0$  [12]. It follows that there is an infinite number of parameter pairs  $(p^2, A'_\mu)$  on curves  $A'_\mu(p^2)$ . Those pairs  $(p^2, A')$  for which the Eqs. (18) and (19) have simultaneous solutions can then be determined in the same way as for the similar equations in the case of the  $H_2^+$  molecule ion (cf. e.g. [1]).

b) Case with  $Z_1 = Z_2 = 0$

In the case that there are no Coulomb centres (or in the case of equal opposite charges  $R(Z_1 + Z_2) = 0$ ) Eq. (23) goes over into the differential equation of the associated Légendré functions. Its solutions  $P_n^m(\mu)$  and  $Q_n^m(\mu)$  have

$$\begin{aligned} \text{for } 2Q + A'_0 + p_0^2 \leq 1/4 & \quad \text{no zeros in } (1, \infty), \\ \text{for } 2Q + A'_0 + p_0^2 > 1/4 & \quad \text{infinitely many zeros in } (1, \infty) \end{aligned}$$

(cf. e.g. [13]). From the number of zeros now again follows the number of eigenvalues  $\alpha$  below the limit  $\alpha_0$  of the non-discrete part of the spectrum [12]:

$$2Q + A'_0 + p_0^2 \leq 1/4: \quad \text{no eigenvalues below } \alpha_0, \quad (24)$$

$$2Q + A'_0 + p_0^2 > 1/4: \quad \text{infinitely many eigenvalues below } \alpha_0. \quad (25)$$

Corresponding to the number of eigenvalues below  $\alpha_0$  there are parameter pairs  $(p_0^2 - \alpha \cos\theta, A'_0 + \alpha \sin\theta)$ , with  $\alpha < p_0^2/\cos\theta$  for which there are solutions of the  $\mu$ -Eq. (18). If the greatest value of  $A'_0$  and the lowest value of  $p_0^2$  on one  $A'_\nu(p^2)$ -curve in the range  $p^2 \geq 0$  are inserted into the inequalities (24) and (25), one can decide if, on the special  $A'_\nu(p^2)$ -curve ( $m$  given, for a certain  $l = m, m + 1, \dots$ ) under consideration there are any possible parameter pairs  $(p^2, A')$  for *both* differential Eqs. (18) and (19). Accordingly there will be eigenvalues  $-p^2$  of the partial differential Eq. (17) (cf. Fig. 1 for the following discussion).

In the case  $Z_1 = Z_2 = 0$  the above mentioned extremal pair on one  $A'_\nu(p^2)$ -curve is  $(0, -l(l+1))$  [14]. It follows then: if one has

$$-l(l+1) \leq 1/4 - 2Q \quad (26)$$

there are no parameter pairs  $(p^2, A')$  corresponding to these values of  $Q$  and  $l$ , and thus there are no energy eigenvalues  $E$ , which are determined by  $p^2$ .

If one has

$$-l(l+1) > 1/4 - 2Q \quad (27)$$

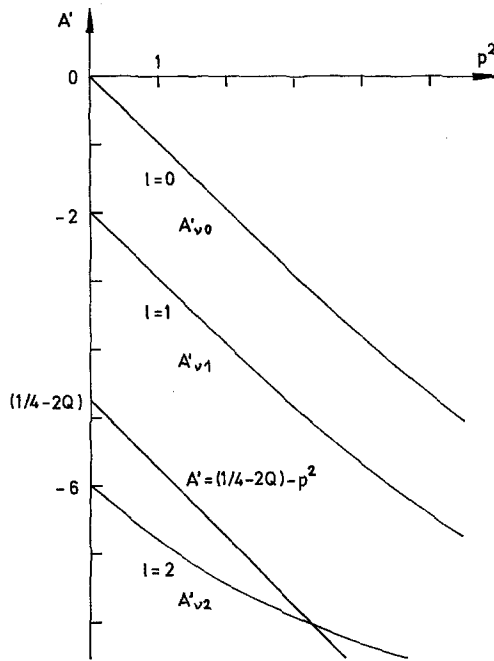


Fig. 1. The qualitative behaviour of the functions  $A'_{v,l}(p^2)$

there are infinitely many parameter pairs  $(p^2, A')$  for these values of  $Q$  and  $l$ , which lie below the straight line  $A'(p^2) = -l(l+1)$ . The whole curve  $A'_v(p^2)$  belonging to  $m$  and  $l$  lies above the straight line  $A'(p^2) = (1/4 - 2Q) - p^2$  with the gradient  $-1$ , since  $A'_v(p^2)$  has a gradient with values between  $-1$  and  $0$  (see Eq. (20)). Therefore one always has  $A'_v + p^2 > 1/4 - 2Q$ . The parameter pairs  $(p^2, A')$  above that straight line for which the  $\mu$ - and  $\nu$ -Eqs. (18) and (19) have simultaneous solutions can be determined in a similar way as in the case of the  $H_2^+$  molecule ion (cf. e.g. [1]).

c) Case with  $R(Z_1 + Z_2) \leq 0$  and  $Q \geq 0$

For the remaining cases with  $R(Z_1 + Z_2) \leq 0$  and  $Q \geq 0$  one recognizes from the special case with  $R(Z_1 + Z_2) = 0$  of Eq. (23), that the solutions of the corresponding equation with

$$R(Z_1 + Z_2) + 2Q + A'_0 + p_0^2 \leq 1/4 \quad (28)$$

also have no zeros in  $(1, \infty)$ , since this equation is a Sturm minorant to Eq. (23) for this case [15]. If

$$R(Z_1 + Z_2) + 2Q + A'_0 + p_0^2 > 1/4 \quad (29)$$

the solutions of (23) have at most a finite number of zeros since this behaviour can be shown for the ends of the interval  $(1, \infty)$ . At  $\mu = \infty$  this follows from a



Table 1. Survey of the discrete eigenvalues of the generalized two-centre problem and its limit cases  $R \rightarrow 0$  and  $R \rightarrow \infty$

Value of $Z_1, Z_2$ and $Q$	Inequalities for $Q$ and $l$	$Q(R)$	Potential energy for $0 < R < \infty$	Eigenvalues for the two-centre case	Potential energy for $R=0$	Spectrum below $E=0$ for $R=0^a$	Potential energy for $Z_2 R = \infty$	Eigenvalues for $Z_2 R = \infty^f$
$Z_1=0, Z_2=0$ ( $Q > 0$ ) <sup>a</sup>	$2Q \leq \frac{1}{4} + l(l+1)$	$RC$	$\frac{RC}{r_1 r_2}$	no eigenvalues	0	no eigenvalues	$\frac{C}{r}$	$\frac{C^2}{2n_1^2}$
		$C$	$\frac{C}{r_1 r_2}$	no eigenvalues	$\frac{C}{r^2}$	no eigenvalues	0	no eigenvalues
	$2Q > \frac{1}{4} + l(l+1)$	$RC$	$\frac{RC}{r_1 r_2}$	infinitely many, discrete	0	no eigenvalues	$\frac{C}{r}$	$\frac{C^2}{2n_1^2}$
		$C$	$\frac{C}{r_1 r_2}$	infinitely many, discrete	$\frac{C}{r^2}$	not bounded from below	0	no eigenvalues
$(Z_1 + Z_2) > 0$ ( $Z_1 + Q) > 0^b$	$2Q \leq \frac{1}{4} + l(l+1)$	$RC$	$\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{RC}{r_1 r_2}$	infinitely many, discrete	$\frac{Z_1 + Z_2}{r}$	$\frac{(Z_1 + Z_2)^2}{2n^2}$	$\frac{Z_1 + C}{r}$	$\frac{(Z_1 + C)^2}{2n_1^2}$
		$C$	$\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{C}{r_1 r_2}$	infinitely many, discrete	$\frac{Z_1 + Z_2}{r}$	$E_{nl}^*$	$\frac{Z_1}{r}$	$\frac{Z_1^2}{2n_1^2}$
	$2Q > \frac{1}{4} + l(l+1)$	$RC$	$\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{RC}{r_1 r_2}$	infinitely many, discrete	$\frac{Z_1 + Z_2}{r}$	$\frac{(Z_1 + Z_2)^2}{2n^2}$	$\frac{Z_1 + C}{r}$	$\frac{(Z_1 + C)^2}{2n_1^2}$
		$C$	$\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{C}{r_1 r_2}$	infinitely many, discrete	$\frac{Z_1 + Z_2}{r}$	not bounded from below	$\frac{Z_1}{r}$	$\frac{Z_1^2}{2n_1^2}$
$(Z_1 + Z_2) \leq 0$ $Z_1 \neq Z_2$ ( $Z_1 + Z_2 + Q) \geq 0^c$	$R(Z_1 + Z_2) + 2Q + A_0 + p_0^2 \leq \frac{1}{4}$	$RC$	$\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{RC}{r_1 r_2}$	no eigenvalues	$\frac{Z_1 + Z_2}{r}$	no eigenvalues	$\frac{Z_1 + C}{r}$	$\frac{(Z_1 + C)^2}{2n_1^2}$
		$C$	$\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{C}{r_1 r_2}$	no eigenvalues	$\frac{Z_1 + Z_2}{r}$	no eigenvalues	$\frac{Z_1}{r}$	$\frac{Z_1^2}{2n_1^2}$
	$R(Z_1 + Z_2) + 2Q + A_0 + p_0^2 > \frac{1}{4}$	$RC$	$\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{RC}{r_1 r_2}$	at most a finite number of eigenvalues	$\frac{Z_1 + Z_2}{r}$	no eigenvalues	$\frac{Z_1 + C}{r}$	$\frac{(Z_1 + C)^2}{2n_1^2}$
		$C$	$\frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{C}{r_1 r_2}$		$\frac{Z_1 + Z_2}{r}$	not bounded from below	$\frac{Z_1}{r}$	$\frac{Z_1^2}{2n_1^2}$

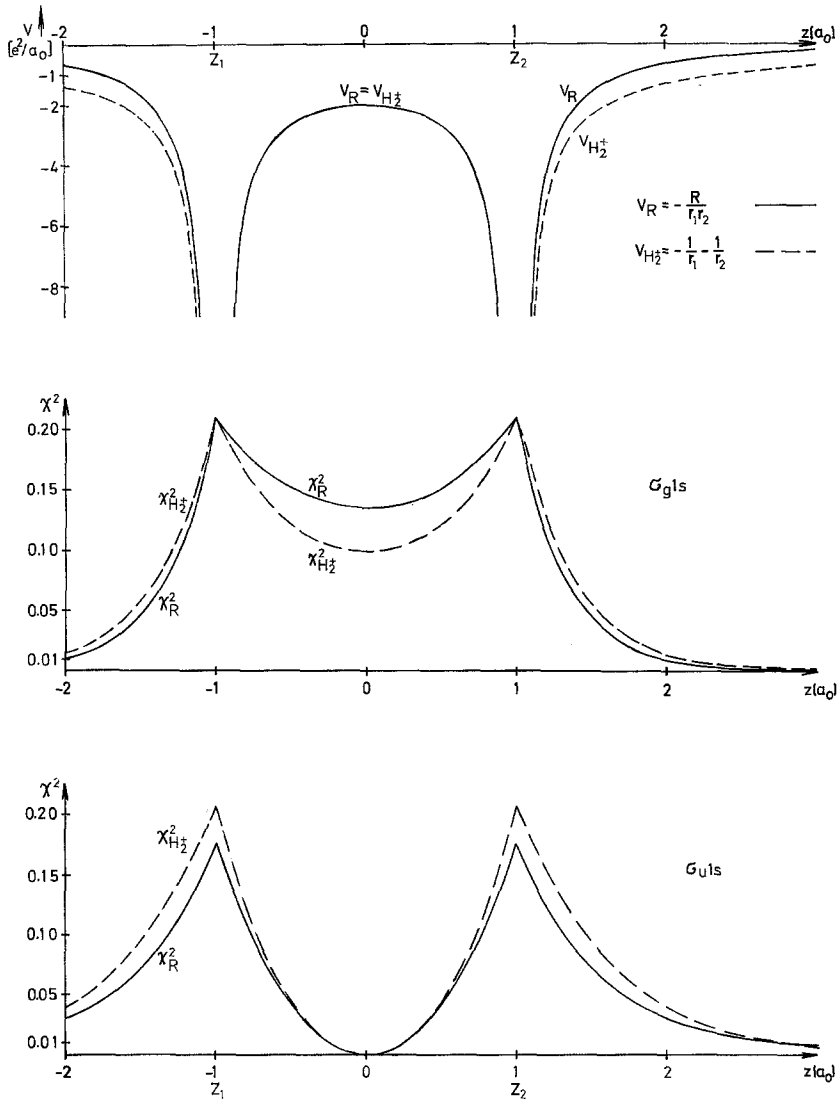


Fig. 2. The potential energy for the case  $V_R = -R/r_1 r_2$  in comparison with the potential energy  $V_{H\frac{1}{2}} = -1/r_1 - 1/r_2$  and the corresponding electron densities along the  $z$ -axis for the two lowest states  $\sigma_g 1s$  and  $\sigma_u 1s$  ( $R = 2[a_0]$ )

Footnotes to Table 1

- <sup>a</sup> In the trivial case  $Q \leq 0$ , no discrete eigenvalues exist.
- <sup>b</sup> This condition has been introduced only for  $R \rightarrow \infty$ : if  $(Z_1 + Q) \leq 0$ , then there are no eigenvalues for  $Q = RC$  in the limit case  $R = \infty$ .
- <sup>c</sup> If  $(Z_1 + Z_2 + Q) < 0$ , no discrete eigenvalues exist.
- <sup>d</sup> Cf. [5].
- <sup>e</sup>  $E_{nl}$  is given e.g. in Eq. (10) of [1].
- <sup>f</sup> Cf. [1].

theorem of Kneser [11]; at  $\mu = 1$  this is true since this point is a regular singular point of the differential equation [16]. Thus it follows in the same way as above that there are at most a finite number of energy eigenvalues below  $E = 0$  for a certain value of  $R(Z_1 + Z_2)$  and  $Q$ . In order to determine these values one has (as above) to insert into Eq. (28) and (29) the highest value of  $A'_v$  and the lowest value of  $p^2$  on one  $A'_v(p^2)$ -curve in the region  $p^2 \geq 0$ . A simple quantitative result as in the case of equal centres  $Z_1 = Z_2 \geq 0$  cannot be presented here, since  $A'_v(p^2)$  of the  $v$ -Eq. (19) does not accept integral values in the limit  $p^2 = 0$ . However the region consisting of pairs  $(R(Z_1 + Z_2), Q)$  with  $R(Z_1 + Z_2) < 0$ , and  $Q \geq 0$  for which bound states still exist can be determined numerically within the scope of the methods described in Part I [1] in the following way. Starting with the initial approximation, that the negative centre has been brought to infinity, the eigenvalues are calculated stepwise for all distances until the limiting value  $p^2 = 0$  has been reached.

The results for the two-centre cases and for the limit cases  $R = 0$  and  $R = \infty$  are summarized in Table 1 for  $Q(R) = RC$  and  $Q(R) = C$ , where  $C$  is a constant.

#### 4. Results for Special Cases of the Generalized Two-Centre Problem

##### a) Results for the Potential Energy $V_R = -R/r_1 r_2$

The potential energy

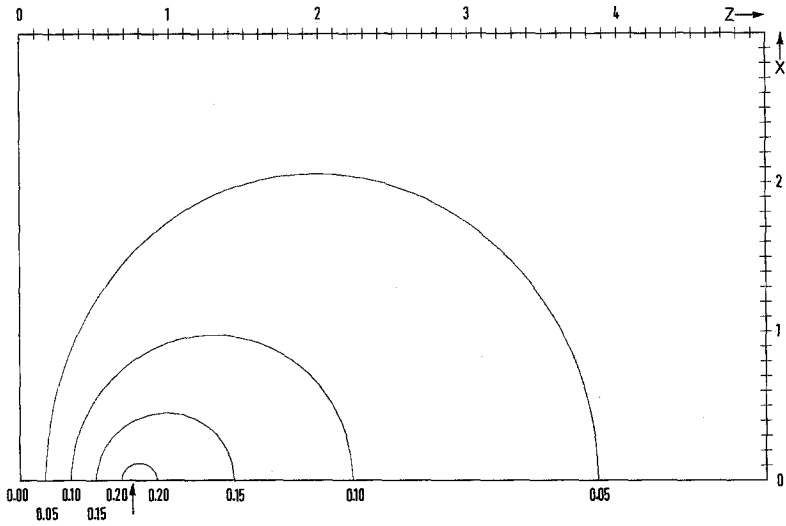
$$V_R = -\frac{R}{r_1 r_2} \quad (30)$$

has the same value as the potential energy of the  $H_2^+$  molecule ion:

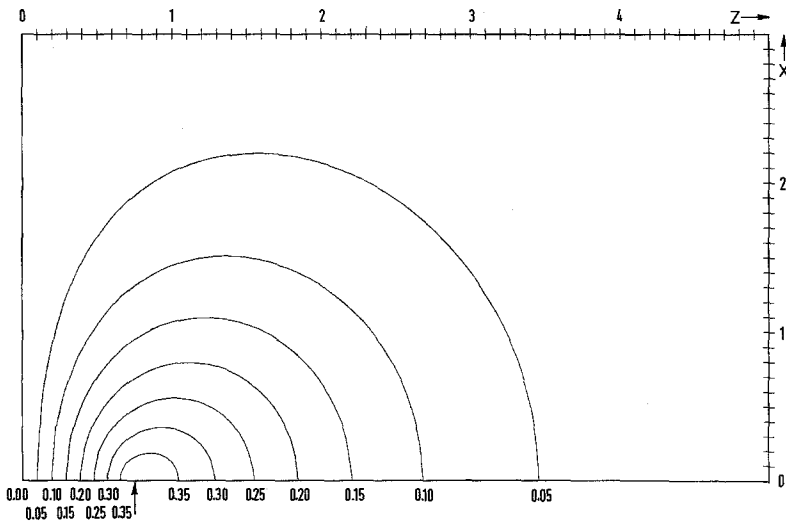
$$V_{H_2^+} = -\frac{1}{r_1} - \frac{1}{r_2} = -\frac{r_1 + r_2}{r_1 r_2} \quad (31)$$

for all those points on the line through the two centres, for which one has  $r_1 + r_2 = R$  (see Fig. 2). In all other points of space where  $r_1 + r_2 > R$  the potential energy  $V_R$  is greater than  $V_{H_2^+}$ . For the ground state  $\sigma_g 1s$  Fig. 2 shows that the electron density  $\chi_R^2$  of the problem with  $V_R$  is greater than the electron density  $\chi_{H_2^+}^2$  of the problem with  $V_{H_2^+}$  in the region  $|z| \leq 1$ . The opposite is true for  $|z| > 1$ . For the first excited states  $\sigma_u 1s$   $\chi_R^2$  is smaller than  $\chi_{H_2^+}^2$  in roughly the region  $|z| \leq 3$ . Since the increase of the electron density between the centres is decisive for a chemical bond (see e.g. [17]) one may conclude here that the potential energy  $V_R$  leads to a strengthening of the bond in comparison to the  $H_2^+$  potential if it is applied in a molecule model.

According to the results of Chapter 3 no bound states exist if in the case of  $l = 0$  the distance  $R$  is not greater than the critical value  $R_{\text{krit}} = 0.125$ , while in the case  $l = 1$  the critical value is  $R_{\text{krit}} = 1.125$ . Assuming a value of  $R (= 1.5)$  near the critical one for  $l = 1$  Fig. 3 shows that the electron density is more distributed over the whole space in comparison to  $H_2^+$ . For  $l = 0$  where this value of  $R$  is far from the critical value 0.125 no such behaviour occurs.



a



b

Fig. 3 a and b. Contour diagram of the wavefunction for the lowest excited state  $\sigma_u 1s$  for a) the problem with the potential energy  $V_R = -R/r_1 r_2$ ; b) the hydrogen molecular ion  $H_2^+$  ( $R = 1.5 [a_0]$ )

For this potential the electronic energy  $E = E(R)$  for the ground state  $\sigma_g 1s$  and the first excited state  $\sigma_u 1s$  has been computed (Fig. 4). The calculations show that for  $R \rightarrow R_{\text{krit}}$  the energy  $E(R)$  tends to zero. For comparison the corresponding energy curves of  $H_2^+$  have been inserted into Fig. 4 too.

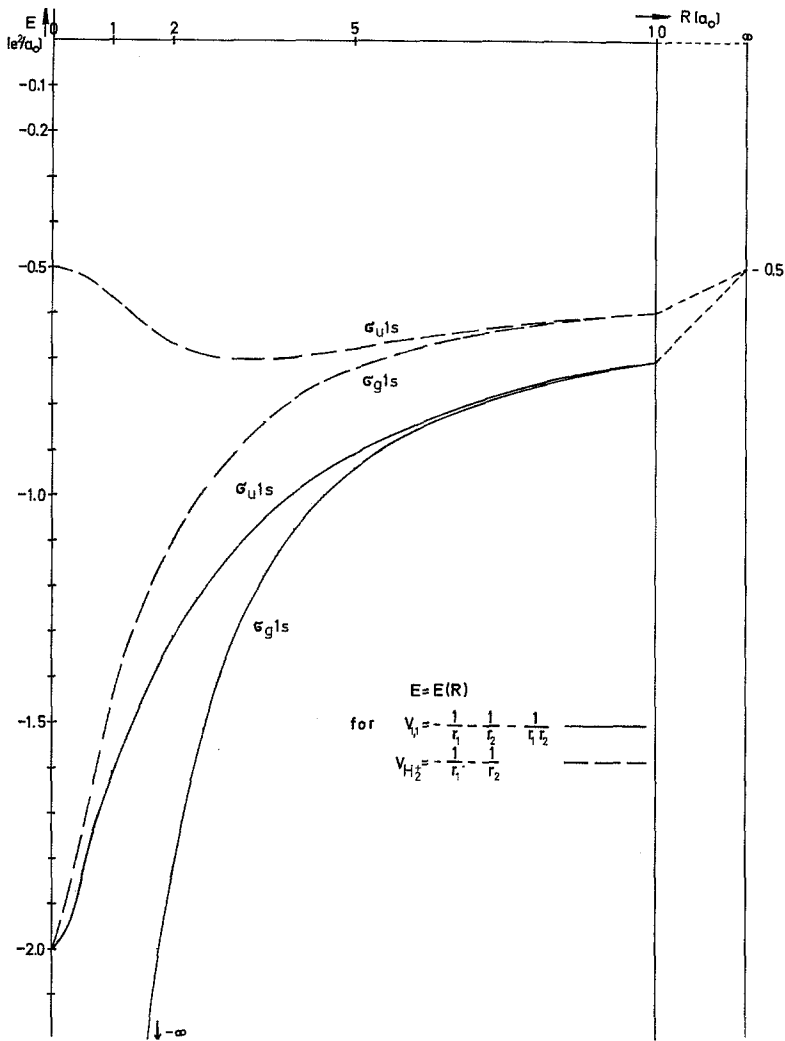


Fig. 4. The energy  $E = E(R)$  for the states  $\sigma_g 1s$  and  $\sigma_u 1s$  for the problem with the potential  $V_R = -R/r_1 r_2$  (For comparison  $E(R)$  of  $H_2^+$  for these states is given too)

*b) Results for the Potential Energy  $V_1 = -1/r_1 r_2$*

The value of  $Q(R) = \text{const} = 1$  in the potential energy:

$$V_1 = -\frac{1}{r_1 r_2} \quad (32)$$

is below the critical value  $Q_{\text{krit}} = 1.125$  for  $l = 1$ . However, for  $l = 0$  the value of  $p$  which does not depend on  $R$  here can be calculated by the methods of Part I [1].  $E(R)$  becomes then the very simple function:

$$E(R) = -\frac{2p^2}{R^2} = -\frac{\text{const}}{R^2} \quad (33)$$

which indeed shows the predicted behaviour for the limiting cases: for  $R \rightarrow 0$  the energy spectrum is not bounded from below ([5]; see Table 1) while for  $R \rightarrow \infty$   $V_1$  disappears and with it the discrete energy spectrum.

c) Results for the Potentials of a) and b) with Additional Coulomb Centres

For the potential energy from a) with additional Coulomb centres:

$$V_{1,1} = -\frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_1 r_2} \tag{34}$$

the first excited state  $\sigma_u 1s$  ( $l=1$ ) has a finite energy eigenvalue even for  $R=0$ , while for  $l=0$  it can be seen that the energy spectrum is not bounded from below

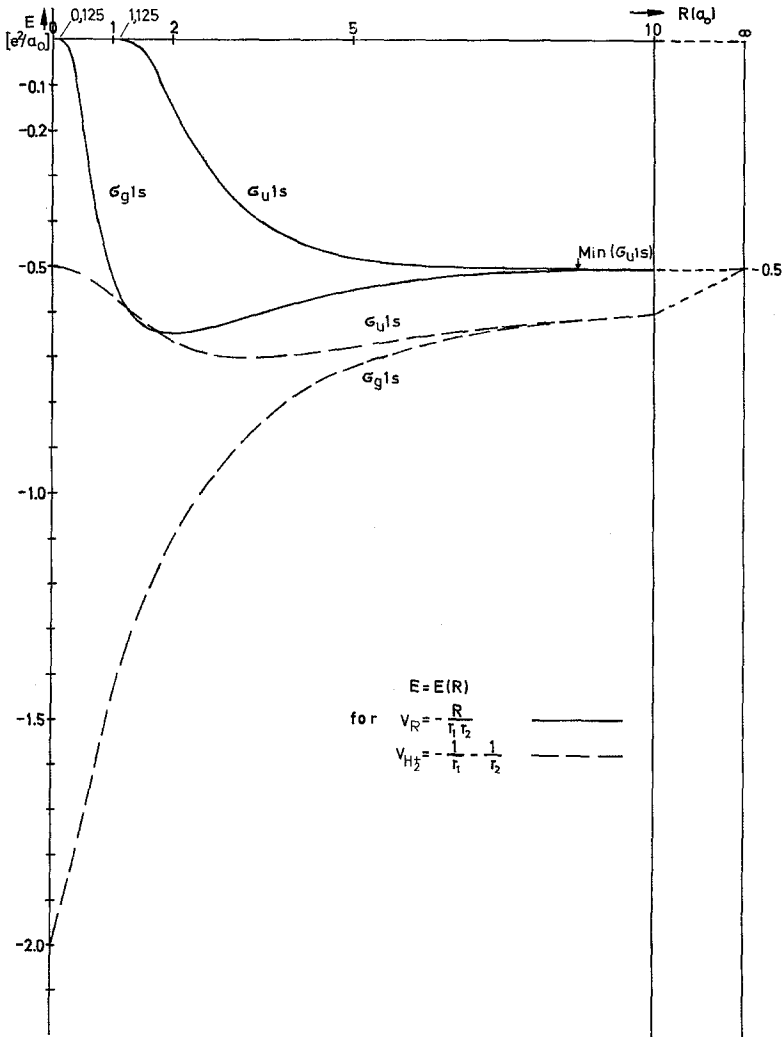


Fig. 5. The energy  $E = E(R)$  for the states  $\sigma_g 1s$  and  $\sigma_u 1s$  for the problem with the potential energy  $V_{1,1} = -1/r_1 - 1/r_2 - 1/r_1 r_2$  (For comparison  $E(R)$  of  $H_2^+$  for these states is given too)

at  $R=0$ . Fig. 5 shows this behaviour with the help of the calculated energy function  $E = E(R)$ .

In the case of the potential energy operator:

$$V_{1,R} = -\frac{1}{r_1} - \frac{1}{r_2} - \frac{R}{r_1 r_2} \quad (35)$$

there are discrete energy eigenvalues for all values of  $l$  and  $R$  as indicated in Table 1. In the limit  $R=0$  the united atom is the same as in  $H_2^+$ , since the linear term in  $R$  disappears. On the other hand the limit cases for both problems for  $R \rightarrow \infty$  are quite different. Especially remarkable is the deep minimum in the energy curve  $E = E(R)$  as shown in Fig. 6 for the ground state of the problem with  $V_{1,R}$ .

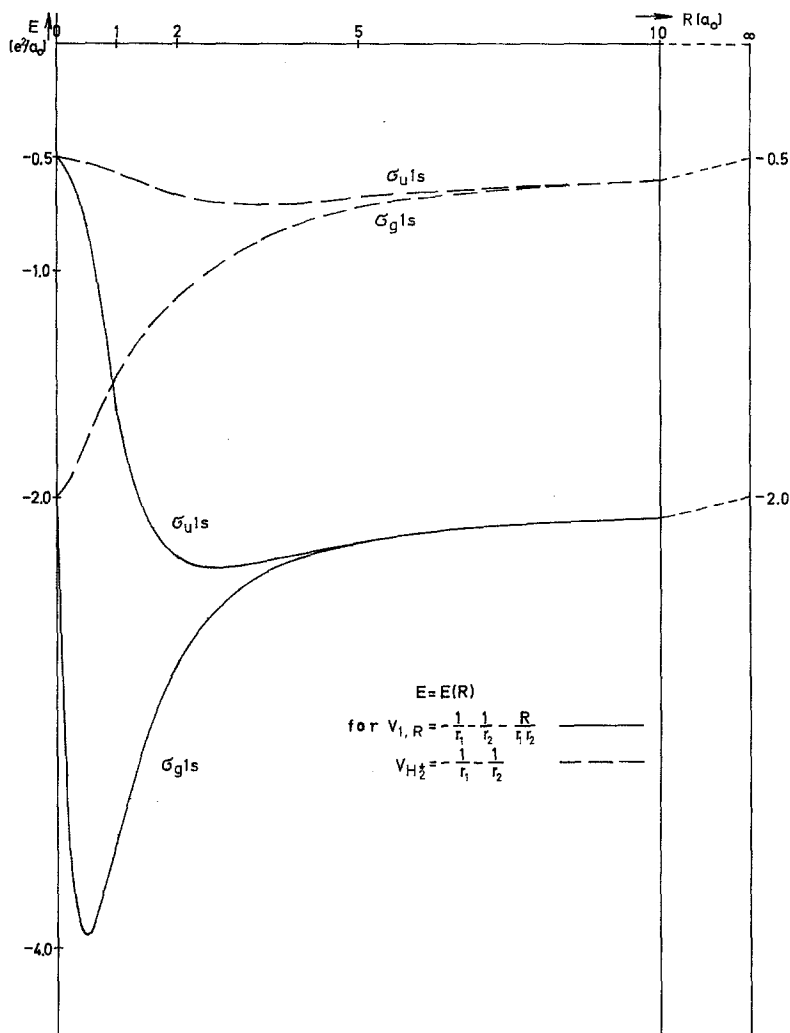


Fig. 6. The energy  $E = E(R)$  for the states  $\sigma_g 1s$  and  $\sigma_u 1s$  for the problem with the potential energy  $V_{1,R} = -1/r_1 - 1/r_2 - R/r_1 r_2$  (For comparison the energy for these states of  $H_2^+$  is given too)

In the region near  $R=1$  the curve  $E(R)$  shows a similar behaviour as for  $V_{1,1}$ , but finally tends to a finite value for  $R \rightarrow 0$ .

Finally results shall be presented for a special case for which energy eigenvalues exist for all  $R$ . This type of model potential could occur in applications to molecular

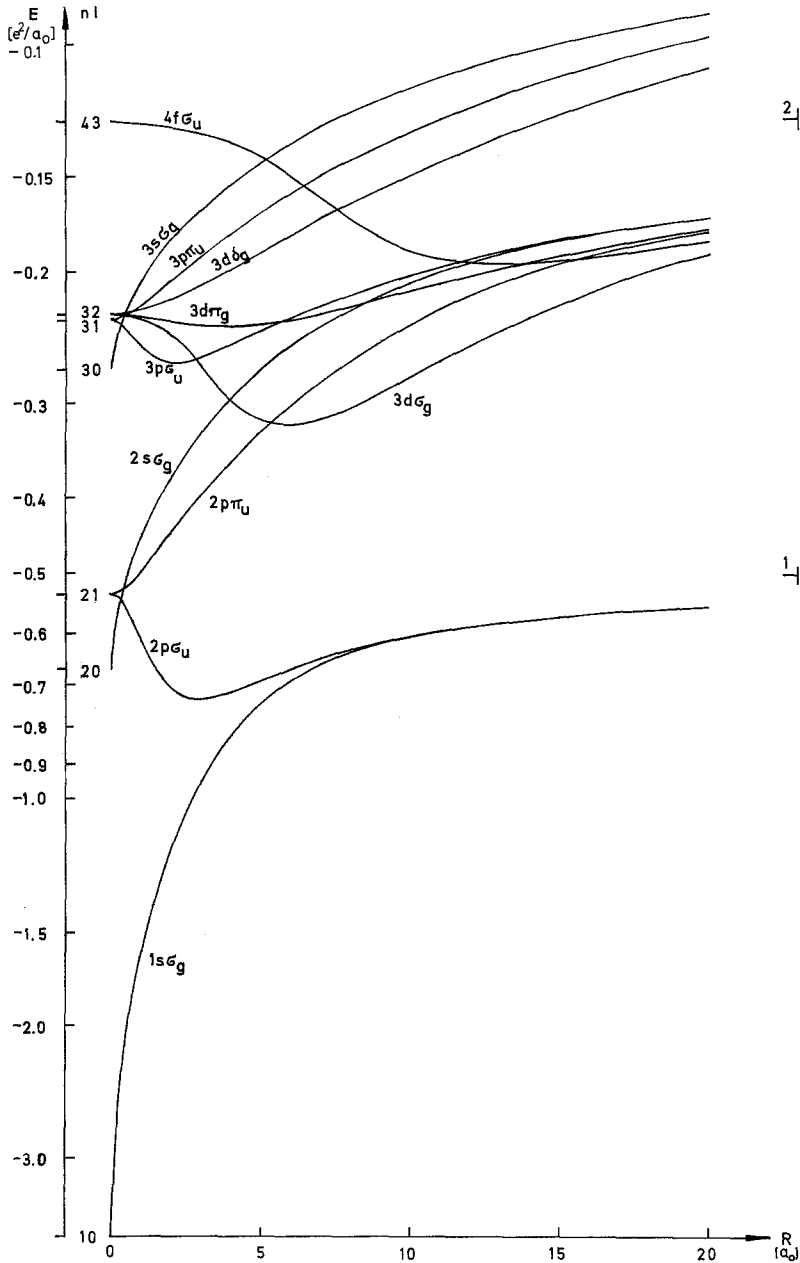


Fig. 7. The energy  $E = E(R)$  for the states with  $n \leq 3$  and for  $4f\sigma_u$  for the problem with the potential energy  $V_{0,1} = -1/r_1 - 1/r_2 - 0.1/r_1 r_2$



Table 2. *The crossing points for some lower states with the same symmetry of the problem with the potential energy  $V(r) = -1/r_1 - 1/r_2 - 0.1/r_1 r_2$  (see Fig. 7)*

States	$R$ [a.u.]	$-E$ [a.u.]	$-A'$
$3s\sigma_g$	0.42	0.22890	0.0135
$3d\sigma_g$			6.0102
$2s\sigma_g$	3.95	0.29442	1.4459
$3d\sigma_g$			7.1566
$3p\sigma_u$	11.71	0.19447	6.3018
$4f\sigma_u$			18.9187

problems. As an example the case with  $Z_1 = Z_2 = 1$  and  $Q = 0.1$  shall be discussed. The correlation diagram for the states with principal quantum numbers 1 to 3 and for the state  $4f\sigma_u$  (classification according to the united atom case) are shown in Fig. 7. The energy values  $E_{nl}$  can be calculated for  $R = 0$  with the formula (10) of Part I [1]. In the region near  $R = 0$  the state  $2p\sigma_u$  lies above the state  $2s\sigma_g$ . These two energy curves cross at about  $R = 0.3$ , and the state  $2s\sigma_g$  remains then for the whole region of  $R$  above the state  $2p\sigma_u$  (see Fig. 7). In the case of an additional repulsive force  $2p\sigma_u$  lies below  $2s\sigma_g$  for all  $R$ .

One should note that there appear also in this case as in other two-centre problems (cf. e.g. [1]) some crossing points of the energy curves for states with the same symmetry (see Fig. 7). Some of these are listed in Table 2. It seems to be remarkable that in this case also the curves for states of equal main quantum number  $3s\sigma_g$  and  $3d\sigma_g$  do cross.

The curve of the one-electron energies for  $C = 0.1$  reminds on that of the system He-He, for which the united atom Be has a total configuration  $(1s)^2(2s)^2$  (see e.g. [17]). Therefore for the system He-He the configurations  $(1s\sigma_g)^2(2p\sigma_u)^2$  ( $R$  large) and  $(1s\sigma_g)^2(2s\sigma_g)^2$  ( $R$  small) will have to be considered (Fig. 7).

#### d) *The Connection of Generalized Two-Centre Orbitals with Slater-Zener-Type Orbitals*

The Slater-Zener-type orbitals:

$$\chi_0 = N r^{n^*-1} e^{-\frac{Zr}{n^*}} Y_l^m(\theta, \phi) \quad (36)$$

are those solutions of the problem (2) which have no zeros in their radial part, and for which especially:

$$Q_0 = -n^*(n^* - 1)/2 + l(l + 1)/2. \quad (37)$$

These orbitals may be generalized to the two-centre case with equal centres as those special solutions of the problem:

$$\left( -\frac{A}{2} - \frac{Z/2}{r_1} - \frac{Z/2}{r_2} - \frac{-n^*(n^* - 1)/2 + l(l + 1)/2}{r_1 r_2} \right) \chi = E\chi \quad (38)$$

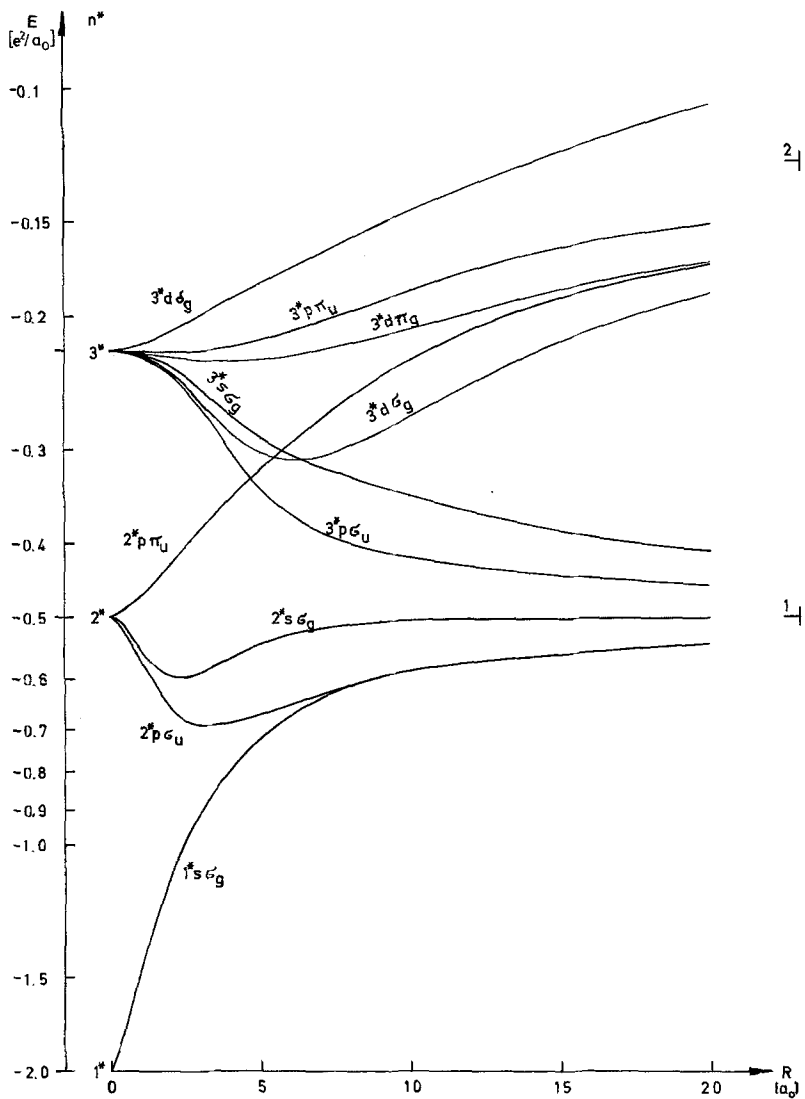


Fig. 8. The energy  $E = E(R)$  for the problems with a potential, which goes over into a Slater-type potential for  $R \rightarrow 0$  for the states with  $n^* \leq 3$

Table 3. The values of  $Q$  for the generalized Slater-Zener-type orbitals, which are plotted

United atom-designation $n^*lm$	Value of the parameter $Q$
$1^*s\sigma_g$	0
$2^*s\sigma_g$	-1
$2^*p\sigma_u$	0
$2^*p\pi_u$	0
$3^*s\sigma_g$	-3
$3^*p\sigma_u$	-2
$3^*p\pi_u$	-2
$3^*d\sigma_g$	0
$3^*d\pi_g$	0
$3^*d\delta_g$	0

which have no zeros in their  $\mu$ -part. Vor  $R \rightarrow \infty$  (38) goes over into a hydrogenic problem [1]. Correlation diagrams for some examples of Slater-type problems are shown in Fig. 8. The values of the parameter  $Q_0$  for the generalized Slater-Zener-type functions are given in Table 3 for the plotted energy curves. If  $Q_0 = 0$  then  $n^* = n$  and the problem is reduced to that of the  $H_2^+$  molecule ion.

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