

SIMULATION OF THE INFLUENCE OF CORE ELECTRONS BY A PSEUDOPOTENTIAL II*

APPLICATIONS TO SOME MOLECULES WITH TWO AND THREE ATOMS

By

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(Received 20. II. 1969)

Pseudopotential theory is combined with the Hartree—Fock and natural expansion method to calculate the molecular constants D_e , R_e and k_e for Na_2 , K_2 , NaCs and BeH_2 . We treat these molecules as two- or four-electron problems respectively in the pseudopotential field of their cores. We then analyze the energies and wave functions in terms of the contributions of the different natural orbitals to the correlation energy. The calculated equilibrium distances agree well with the experimental ones. The dissociation energies are in better agreement with experiment than those of previous calculations.

1. Introduction

Ab initio calculations are at present possible with rather high accuracy for small molecules and with modest accuracy for large molecules.

On the other hand — since the early days of quantum chemistry — the obvious similarities in the chemical and spectroscopical behaviour of the elements of one column of the periodic system have encouraged people to simplify many-electron theory by dividing the electrons into core and valence electrons [1]. If one limits oneself to a treatment of the valence electrons of an atom or molecule one has to account for a twofold influence of the inner electrons. On one hand they shield part of the nuclear charge for the valence electrons, on the other hand the Pauli principle requires that the valence orbitals are orthogonal to the core orbitals.

The last requirement has already been recognized in 1935 by H. HELLMANN [1] and P. GOMBÁS [2] who independently developed the concept of pseudopotential theory. They started from expressions for the pseudopotential in terms of the electron density ρ of the core electrons based on the Thomas-Fermi model. Whereas GOMBÁS refined his expressions and replaced the statistical electron density ρ by its quantummechanical analogue [3] HELLMANN chose an analytic 'ansatz' with adjustable parameters. He started from the observation that the kinetic and potential energies of a valence-electron cancel to a high extent inside the core region. The logical consequence of this argument would have been to use a cut-off Coulomb potential (cf. Equ. (4)).

* Dedicated to Prof P. GOMBÁS on his 60th birthday.

For other reasons HELLMANN preferred the following analytical form of the pseudopotential:

$$W(r) = -\frac{Z'}{r} + A \frac{e^{-\kappa r}}{r}, \quad (1)$$

where Z' , A and κ are parameters which are adjusted such that the lowest states of the atom are well reproduced. This potential (1) is still being applied [4], but during the last few years many other types of pseudopotentials have been discussed in the literature. With the potential

$$\begin{aligned} W(r) &= -\frac{Z_R}{r}, & r > R_c, \\ &= \infty, & r < R_c, \end{aligned} \quad (2)$$

where R_c is the core radius and Z_R the reduced nuclear charge R. PARSONS and V. WEISSKOPF [5] obtained surprisingly good results for the Rydberg series of alkali atoms. An alternative but related potential is that used by B. J. AUSTIN and H. HEINE [6]

$$\begin{aligned} W(r) &= -\frac{Z_R}{r}, & r > R_c, \\ &= 0, & r < R_c, \end{aligned} \quad (3)$$

in a qualitative discussion of atomic properties in relation to the periodic system. As the discontinuity of this potential at R_c does not seem to be very physical the present authors preferred the so-called 'cut-off' potential

$$\begin{aligned} W(r) &= -\frac{Z_R}{r}, & r > R_c, \\ &= -\frac{Z_R}{R_c}, & r < R_c. \end{aligned} \quad (4)$$

In the first part of this series [7] (hereafter referred to as part I) we have used this potential to calculate Rydberg series of alkali-atoms, alkali-like positive ions and ground- and excited states of atomic two-valence electron systems (Be, Mg, Ca).

Rather than to use one of those pseudopotentials that contain adjustable parameters one can also use (as SZASZ and MCGINN [4e] have done for atoms and for molecules) the pseudopotential (Equ. (6)) derived by PHILLIPS and KLEINMANN [8] on the grounds of rigorous quantum mechanics. It turns out

that the behaviour of the pseudopotential inside the core is relatively irrelevant as far as the total energy of the valence electrons in this field is concerned. As A. U. HAZI and S. A. RICE [9] have pointed out, the agreement of the pseudopotential eigenvalues with the correct orbital energies depends more significantly on the proper boundary conditions imposed on the wave function by the pseudopotential than on the behaviour inside the core. This is consistent with the observation (see part I) that pseudopotentials which are very different inside the core lead to quite similar results.

The pseudopotentials just discussed (except the HELLMANN potential*) can be regarded as special cases of the general expression:

$$\begin{aligned} W^n(r) &= \sum_{\nu=0}^n a_{\nu} r^{\nu}, & r < R_c, \\ &= -\frac{Z_R}{r}, & r > R_c. \end{aligned} \quad (5)$$

By choosing the parameters of this potential appropriately one may hope to combine the advantages of the different types just mentioned. The computation of the necessary matrix elements of this potential with a basis of Gaussian-functions is straightforward (see the Appendix), which is important for the applicability to molecules.

2. General theory

a. Choice of the pseudopotential

If, in the atomic case, one wants to take care of the orthogonality of the valence-orbitals to the core orbitals in a quantum-mechanically straightforward way one may use the PHILLIPS—KLEINMANN potential [8]

$$W = U + \sum_{\alpha=1}^{\nu-1} (\epsilon_{\nu} - \epsilon_{\alpha}) |\Phi_{\alpha}\rangle\langle\Phi_{\alpha}|. \quad (6)$$

Here U denotes a Coulomb-potential of the atoms, Φ_{α} are the core orbitals with orbital energies ϵ_{α} and with valence orbital energy ϵ_{ν} . Although the derivation of this potential is based on a one-electron model it can also be justified [9], [4b], [4c] in the framework of Hartree—Fock theory. This pseudopotential contains a non-local operator which projects a given function on the core orbitals.

* Note, however, that for $n = 2$ the potential (5) is very close to the HELLMANN potential (1).

The question whether it is justified to replace the correct non-local pseudopotential by a local model potential has been discussed by several authors [4b, 4c, 5, 9]. Actually the model potentials mentioned in the Introduction are either local or just l -dependent, i.e. of the form

$$W = \sum_{l=0} W_l P_l, \quad (7)$$

where P is the projection operator on the subspace of orbitals with angular quantum number l . (see also [23]).

Now the question arises how to choose the corresponding pseudopotential for a molecule. As a first approximation one expects it to be a sum of atomic contributions. This question has recently been discussed by SCHWARZ [18] and HAZI and RICE [9c]. (As to earlier work on this question see HARRISON [19] and GOMBÁS [3]). In fact there are only very few practical experiences concerning the relation of the molecular and atomic pseudopotentials and about the role of correction terms [18]. Most practical applications of the pseudopotentials deal with atomic states or solids [21], [9b], [18], except for HELLMANN'S early molecular calculations [1]. So far only SZASZ and MCGINN [4e] (see also PREUSS [20]) have contributed to the study of molecular binding, using a pseudopotential approach, namely for the molecules Li_2 , Na_2 , K_2 , LiH , NaH , and KH . The results of these authors encourage one to construct the molecular pseudopotential from those of the constituent atoms. We regard it as sufficiently justified to write our molecular model potential in the form

$$\begin{aligned} W^n(r_{i\alpha}) &= \sum_{\alpha} W_{\alpha}^n(|\mathbf{r}_i - \mathbf{r}_{\alpha}|) = \sum_{\alpha} \sum_{\nu=0}^n a_{\nu}^{\alpha} |\mathbf{r}_i - \mathbf{r}_{\alpha}|^{\nu}, \quad r_i < R_c^{\alpha, n} \\ &= - \sum_{\alpha} \frac{Z_{\alpha}^{\alpha}}{|\mathbf{r}_i - \mathbf{r}_{\alpha}|}, \quad r_i > R_c^{\alpha, n} \end{aligned} \quad (8)$$

for the i -th electron, where α labels the nuclei, where the a_{ν}^{α} are semiempirical parameters and where n , the degree of the polynomial, is fixed in advance. In fact, we only consider the possibilities $n = 0$ and $n = 1$, i.e. we chose either a cut-off Coulomb-potential (W^0) or a potential with a linear repulsive part inside the core region (see Fig. 1).

In part I we have limited ourselves to W^0 , i.e. the cutoff Coulomb potential. The results were rather satisfactory for the atomic calculations. However, we found that the second and third s -type Rydberg states were not too well reproduced and that the 'radii' of the ions were somewhat too large. In order to remedy these slight defects we have started investigations with the more general type (8) of pseudopotential which in fact led to still better agreement for the Rydberg series and to smaller 'ionic radii'. Whereas in atoms the non-local properties of the pseudopotential can to some extent be accounted for

by the l -dependent form of Equ. (7), for molecules the use of such angular-dependent atomic pseudopotentials in the sum (8) would mean great computational difficulties. Calculation of the matrix elements would imply that every basis orbital has to be expanded in terms of spherical harmonics with respect to any of the present nuclei. In order to avoid these difficulties we have used local (i.e. l -independent) atomic contributions to the potential, namely those that are appropriate for s -orbitals. In the case of Li and Na the p -orbitals (and of course d and higher orbitals) should have a more attractive potential (i.e. a smaller

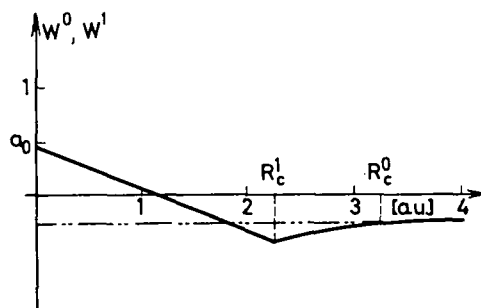


Fig. 1. Pseudopotentials W^0 and W^1 for Na (in correct scale)

cut-off radius). So by using the pseudopotential appropriately for s -orbitals the contribution of the p -orbitals is expected to be underestimated. This should result in an increase of the energy value like that due to the use of a poorer basis. For K, Rb and Cs the cut-off radii corresponding to s - and p -orbitals do not differ much so that a local potential is justified as long as d -contributions to binding are negligible.

We do not, however, regard the local approximation as completely satisfactory and work is in progress to account for the l -dependence of the atomic pseudopotential in molecular calculations.

In connection with pseudopotential theory the question arises how one should represent the repulsion of the cores. If the cores are rigorously non-overlapping it is justified to replace them by point charges. So far we have not considered effects due to an overlap of the cores. They are supposed to depend exponentially on the distance and to be non-negligible only for very short interatomic distances.

b. Natural orbital expansions and their combination with the pseudopotential method

Since by using the pseudopotential method we are left with a rather small number of valence electrons, we can therefore treat this small number by rather sophisticated methods which would not be manageable in a treatment of all

electrons. Let us start with the Hamiltonian for the valence electrons

$$H = -\frac{1}{2} \sum_i (\Delta_i - \sum_{\alpha} W_{\alpha}^n(r_{i\alpha})) + \sum_{i,j} \frac{1}{r_{ij}} \quad (9)$$

in which $\sum_{\alpha} W_{\alpha}^n$ stands for the potential of Equ. (8). The HF equations for a valence electron in a closed shell state will then be

$$\left[-\frac{1}{2} \Delta_i - \sum_{\alpha} W_{\alpha}^n(r_{i\alpha}) + \sum_j (2J^j - K^j) \right] \Phi_i = \epsilon_i \Phi_i, \quad (10)$$

where J^j and K^j are the Coulomb and exchange operators, respectively and Φ_i is a HF pseudo-orbital.

In order to compare the calculated total energies with their experimental counterparts one has to note that the zero of the energy scale corresponds to the sum of the core energies, i.e. the sum of the energies of the ions obtained from the neutral atoms by ionizing off all the valence electrons.

In part I we have obtained good agreement for the orbital energies and the total valence-electron energies between complete Hartree—Fock calculations and HF calculations in the field of a pseudopotential. This agreement turns out to hold in our molecular calculations as well. If we want to get even better agreement with experiment we have, of course, to go beyond the Hartree—Fock approximation. This is why we combined the pseudopotential approach with a CI-calculation in terms of approximate natural orbitals like it has been applied in all electron calculations [13c].

The equations to be solved for a two-valence electron system are those derived previously [13a, b]

$$\begin{aligned} (h + J') \chi_1 &= \lambda_{11} \chi_1, \\ Q_i [n_i(h + K^i) + K^i] Q_i \chi_i &= \lambda_{ii} \chi_i, \quad i \neq 1. \end{aligned} \quad (11)$$

Here χ_1 is the 'strongly' occupied (spinfree) natural orbital, χ_i is a 'weakly' occupied one, Q_i a projection operator projecting onto the subspace which is orthogonal to the first $(i-1)$ natural orbitals. h is the one-electron part of the Hamiltonian containing here the pseudopotential, J^i and K^i are Coulomb and exchange operators originating from an electron pair in the space orbital χ_i . $(1k|k1)$ is an exchange integral involving orbital χ_1 and χ_k . The coefficients c_i in the natural expansion of a two-electron function*

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_i c_i \chi_i(1) \chi_i^*(2) \quad (12)$$

* For a generalization to systems with more than two electrons, see [13b].

are finally obtained from the secular equations

$$2c_i h_{ii} + \sum_k c_k (ik|ki) = \mu c_i. \quad (13)$$

The lowest eigenvalue of these equations is the ground-state energy of a two-electron system in the pseudopotential. The equations are solved algebraically, each natural orbital (NO) being represented as a linear combination of a given orthonormal set of one-electron basis functions which are constructed from Gaussian-type orbitals φ . We therefore have to evaluate the matrix elements $(\varphi_a, W_c^n, \varphi_b)$ with respect to the pseudopotential W_c^n .

c. Calculation of the matrix elements

The only matrix elements not known from the literature are those involving the pseudo-potential W_c^n . As basis set for the expansion of the pseudo-orbitals χ_i we use Gaussian-type functions of the form

$$\varphi_\mu = \left(\frac{2\alpha_\mu}{\pi} \right)^{3/4} \exp[-\alpha_\mu(\mathbf{r} - \mathbf{r}_\mu)^2] \quad \mu = a, b, c, \dots \quad (14)$$

The following matrix elements have to be calculated

$$W_{ab,c} \stackrel{\text{def}}{=} (\varphi_a, W_c^n \varphi_b), \quad (15)$$

where W_c^n stands for the pseudopotential. In this Section we only give the final expression (for a detailed description of the evaluation see Appendix A).

$$\begin{aligned} W_{ab,c} = & \sqrt{\frac{\gamma}{\pi}} S_{ab} \left\{ \frac{a_0}{2} \sqrt{\frac{\pi}{\gamma}} [\operatorname{erf}(\sqrt{\gamma}(r_{cp} + R)) - \operatorname{erf}(\sqrt{\gamma}(r_{cp} - R))] + \right. \\ & + \frac{Z_R}{2r_{cp}} \sqrt{\frac{\pi}{\gamma}} [\operatorname{erf}(\sqrt{\gamma}(r_{cp} + R)) + \operatorname{erf}(\sqrt{\gamma}(r_{cp} - R))] + \\ & + \frac{a_0}{2\gamma r_{cp}} [e^{-\gamma(r_{cp} + R)^2} - e^{-\gamma(r_{cp} - R)^2}] + \\ & + \sum_{\nu=1}^n a_\nu \left[\frac{r_{cp}^\nu}{\sqrt{\gamma}} \left(\int_{-\sqrt{\gamma}r_{cp}}^{\sqrt{\gamma}(R-r_{cp})} e^{-u^2} du + (-1)^\nu \int_{\sqrt{\gamma}r_{cp}}^{\sqrt{\gamma}(R+r_{cp})} e^{-u^2} du \right) + \right. \\ & \left. + \sum_{\lambda=1}^{\nu+1} \binom{\nu+1}{\lambda} r_{cp}^{\nu-\lambda} \gamma^{-\lambda/2+1/2} \left(\int_{\sqrt{\gamma}r_{cp}}^{\sqrt{\gamma}(R-r_{cp})} u^\lambda e^{-u^2} du + (-1)^{\nu-\lambda} \int_{\sqrt{\gamma}r_{cp}}^{\sqrt{\gamma}(R+r_{cp})} u^\lambda e^{-u^2} du \right) \right] \Bigg\}. \end{aligned} \quad (16)$$

In this expression S_{ab} is the overlap integral (φ_a, φ_b)

$$S_{ab} = (\alpha_a \cdot \alpha_b)^{-3/4} A^{3/2} e^{-1/2(r_a - r_b)^2 \cdot A}, \quad (17)$$

$$A = \frac{2\alpha_a \cdot \alpha_b}{\alpha_a + \alpha_b}, \quad \gamma = \alpha_a + \alpha_b,$$

and

$$\mathbf{r}_{cp} = \mathbf{r}_c - \mathbf{r}_p$$

with

$$\mathbf{r}_p = \frac{1}{\gamma} [\alpha_a A_x + \alpha_b B_x, \alpha_a A_y + \alpha_b B_y, \alpha_a A_z + \alpha_b B_z] \quad (18)$$

which is a point on the line between \mathbf{a} and \mathbf{b} where the position vectors of the nuclei are defined by

$$\mathbf{a} = [A_x, A_y, A_z], \quad \mathbf{b} = [B_x, B_y, B_z], \quad \mathbf{c} = [C_x, C_y, C_z]. \quad (19)$$

A further reduction of the integrals in this expression for I is possible if we define $J_\lambda(a, b)$ as

$$J_\lambda(a, b) = \int_a^b u^\lambda e^{-u^2} du.$$

We then obtain the recurrence relation

$$J_\lambda(a, b) = \frac{1}{2} [(\lambda - 2)J_{\lambda-2}(a, b) + a^{\lambda-2} e^{-a^2} - b^{\lambda-2} e^{-b^2}].$$

3. The choice of the parameters for the model potential in the calculations of Na_2 , K_2 , NaCs and BeH_2

Our method is semiempirical in the sense that the pseudopotential contains at least one parameter to be adjusted using experimental data. Our philosophy is to adjust the pseudopotential from data of the constituent atoms (ionization energy and possibly higher Rydberg levels), but not from data of the molecule that we want to calculate or from any related molecule. For one atom in different molecules the same pseudopotential should be used. The number of parameters should be as small as possible. If we use W^0 then a single parameter describes the particular type of (singly positive) core, in W^1 two parameters are necessary to characterize the core, but it turns out that for different alkali atoms the optimum choice is in good agreement with the relation $a_0 = +Z_R/R_c$ so that we are again left with one parameter. R_c is then fitted to the lowest Rydberg states with the resulting values of Table I.

Table I

Rydberg states of Na, K, Cs resulting from the pseudopotential W^1 (all quantities in a.u.)

Molecule	a_0	a_1	R_c	$-E(1s)$	$-E(2s)$	$-E(3s)$	$-E(4s)$
Na	+ 0.44	- 0.399	2.266	(0.18886)	0.07242	0.0380	0.0233
Na (exp.)				0.18886	0.07158	0.0376	0.0231
K	+ 0.34	- 0.236	2.908	(0.15952)	0.06507	0.0351	0.02189
K (exp.)				0.15952	0.06371	0.0344	0.0216
Cs	+ 0.29	- 0.174	3.394	(0.14310)	0.05864	0.0323	0.0205
Cs (exp.)				0.14310	0.0606	0.0333	0.0208

a_0 , a_1 , R_c pseudopotential parameters as defined in Equ. (8). To be fitted at $E(1s)$

4. Results of the calculations

One may wonder why in almost all pseudopotential calculations only molecules like Na_2 , K_2 etc. have been investigated. Actually they play the same role in pseudopotential theory as does the H_2 molecule in all-electron calculations. In the pseudopotential method these molecules can be treated as pseudo- H_2 problems. Just as in H_2 , the $1s$ -pseudo-AO's contribute much more to the binding MO's of the ground state than do any other, in particular p -AO's. It is therefore not too crucial to ignore the l -dependence of the pseudopotential and to use that local approximation which is justified for s -AO's.

NaCs has recently been investigated by W. NEUMANN [22] in molecular beam experiments. This stimulated our interest in a theoretical study of this heteronuclear molecule.

The choice of the orbital basis is suggested by the fact that we are dealing with pseudo- H_2 problems. We actually chose the basis of Gaussians used by HOYLAND [14] in his H_2 calculations omitting, however, the Gaussians with highest α_μ -values which in the genuine H_2 problem take care of the representation of the cusp at the nuclei, but adding some Gaussians with smaller α_μ -values in the binding region as is illustrated in Table II.

Since the pseudopotential does not contain any singularities, the problem of the correct cusp does not matter and a Gaussian basis should be better than in the real H_2 problem. The results of our calculations on diatomics using the two model-potentials W^0 and W^1 can be found in Table III.

The parameters a_0 , a_1 , R_c are taken from Table I. The dissociation energies D_e are obtained from $D_e = |E_{\text{HF+corr}} + 2I_p|$ where $E_{\text{HF+corr}}$ is the sum of HF and the correlation energy of the system. The equilibrium distances r_e have been obtained by 4-th degree polynomial fitting, (see Figs. 2—4), from which

Table III

The computed data for the A_2 , AB-type molecules with the pseudopotentials W^1 and W^0 . All quantities are in atomic units

Molecule	1 R_c	2 a_0	3 a_1	4 $-I_p$	5 $-E_{HF}$	6 $-E_{HF+corr.}$
W^1	Na_2	2.266	0.44138	-0.38963	0.3777	0.3759
	K_2	2.91	0.3438	-0.2364	0.3190	0.3142
	$NaCs$ $\left\{ \begin{array}{l} Na \\ Cs \end{array} \right.$	2.266	0.44138	-0.38963	0.3319	0.3284
		3.39	0.2946	-0.1736		
	Li_2	3.00	$\frac{-1}{3.0}$	0	0.3963	0.3907
W^0	Na_2	3.25	$\frac{-1}{3.25}$	0	0.3777	0.3700
	K_2	4.16	$\frac{-1}{4.16}$	0	0.3190	0.3100
	Li_2	3.00	$\frac{-1}{3.0}$	0	0.3963	0.3907
	Na_2	0.1699	5.78	5.8	0.0216	0.0272
	K_2	0.1401	7.1	7.39	0.0170	0.0192
W^1	$NaCs$ $\left\{ \begin{array}{l} Na \\ Cs \end{array} \right.$	0.1456	6.9		0.0191	
	Na_2	0.1670	5.8	5.8	0.018	0.0272
	K_2	0.1350	7.1	7.39	0.013	0.0192
	Li_2	0.182		3.02	0.0184	0.0419
W^0						-0.0075

a) Experimental data from G. HERZBERG, Molecular Spectra and Molecular Structure, I. Spectra of diatomic Molecules (D. Van Nostrand Co., Inc. New York, 1950)

1. core radius
- 2-3. pseudopotential parameters
4. Sum of ionization potential for the free atoms
5. Total HF energy
6. HF energy plus σ and π correlation energy
7. HF orbital energies [b) for Li_2 the orbital energy is the same in an all-electron calculation]
8. Calculated equilibrium distance
9. Experimental equilibrium distance
10. Calculated dissociation energy (for Li_2 only σ -correlation is included)
11. Experimental dissociation energy
12. HF binding energy of an all-electron calculation according to A. C. WAHL [21 (for Na_2) and G. DAS [25] (for Li_2)

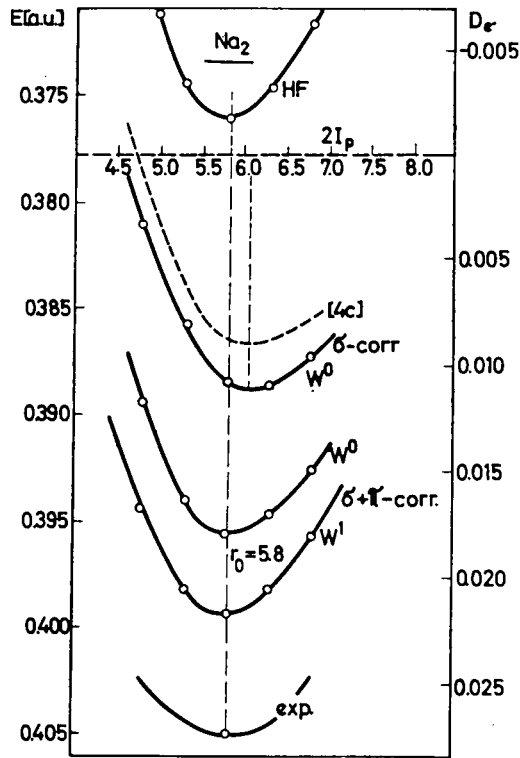


Fig. 2

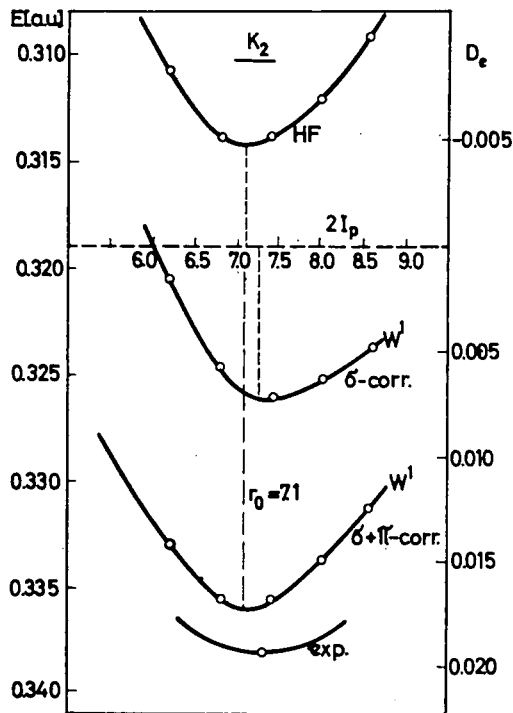


Fig. 3

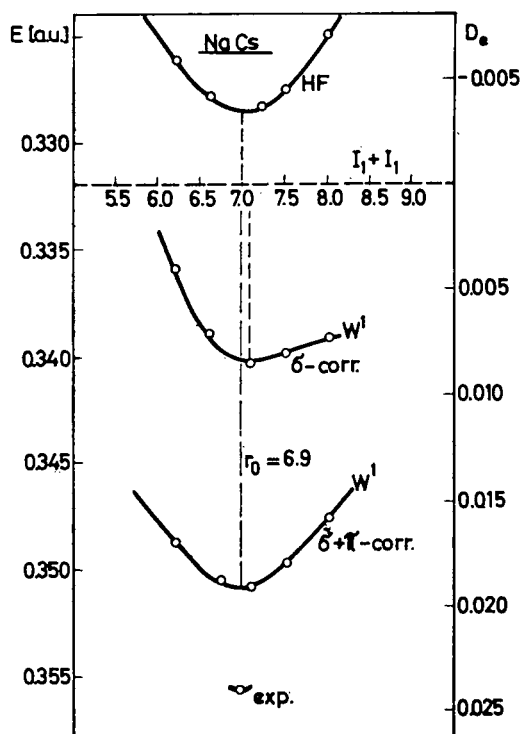


Fig. 4

Figs. 2—4. Energy-potential for Na_2 , K_2 and NaCs as calculated by the pseudopotential method with pseudopotentials W^0 , W^1

HF = Hartree—Fock approximation. σ -corr. = HF + σ -correlation. $\sigma + \pi$ -corr. = HF + $\sigma + \pi$ -correlation. exp. = experimental energy curve which we obtained by subtracting the binding energy D_e (see right hand scale) from the level of the separated atoms (broken line with energy $2I_p$). The curvature corresponds to a quadratic parabola obtained from the experimental force-constant. See [4c]

we obtained the force constants K_e as well. The resulting values are collected in Table IV for different approximations. In comparing the results with their experimental counterparts one sees that the geometry of these systems is already accounted for in the Hartree—Fock approximation like one finds in all-electron HF calculations. The equilibrium distances are increased if one allows for σ -correlation (i.e. by performing CI with configurations constructed from σ -orbitals only) but are decreased again to the correct values if π -correlation is taken into account, too.* (For a more detailed discussion of this problem see [13c]). In fact, the σ -correlation energy contributions increase with distance while the π -correlation decreases with distance, so that the sum of both re-

* A Weinbaum function (Heitler—London function + ionic terms) as used by SZASZ and MCGINN accounts to some extent for σ -correlation (but not for π -correlation). This is the reason for their too large equilibrium distances.

Table IV
Equilibrium distances, force constants and total energies for Na₂, NaCs, K₂

Molecule	approximation	r_e [a.u.] calc.	r_0 [a.u.] exp.	K_e [a.u.] theor.	K_e [mdyn/Å]		$-E_0$ [a.u.]
					theor.	exp.	
Na ₂	SCF	5.8	5.8	0.009	0.14	0.083	0.3759
	SCF + corr.	5.8		0.007	0.11		0.3993
NaCs	SCF	7.0	—	0.0057	0.07	0.051	0.3284
	SCF + corr.	6.9	—	0.0051	0.08		0.3510
K ₂	SCF	7.1	7.39	0.0048	0.075	0.048	0.3142
	SCF + corr.	7.1		0.0045	0.07		0.3360

Table V

Correlation analysis of Na₂ for different distances r . All quantities are in atomic units

r	E_{HF}	$-E(1\sigma_u)$	$-E(1\pi_u^2)$	$-E(2\sigma_g)$	$-E(\sigma + \pi)$
4.8	0.3691	0.00944	0.00686	0.00257	0.02526
5.3	0.3744	0.00807	0.00618	0.00325	0.02368
5.8	0.3759	0.00902	0.00544	0.00353	0.02343
6.3	0.3745	0.01030	0.00477	0.00373	0.02358
6.8	0.3715	0.01193	0.00419	0.00383	0.02414

mains approximately constant as can be seen from the correlation-energy analysis for Na₂ in Table V.

The corresponding natural orbitals which contribute to the correlation energy are plotted in Figs. 5—8 for NaCs. Although the accuracy of these NO's (particularly of those with small expansion coefficients) should not be overestimated these plots are quite illustrative. The broken lines indicate the core region of the corresponding atoms. Inside this region the niveau lines have no physical meaning.

In Table VI the results of our calculations on BeH₂ are summarized for the equilibrium distance $r_{\text{Be-H}} = 2.5$ a.u. for the linear symmetric molecule. The results are somewhat poorer, similar to those which have been found for hydrides in general [4c], a phenomenon which is not yet fully understood.

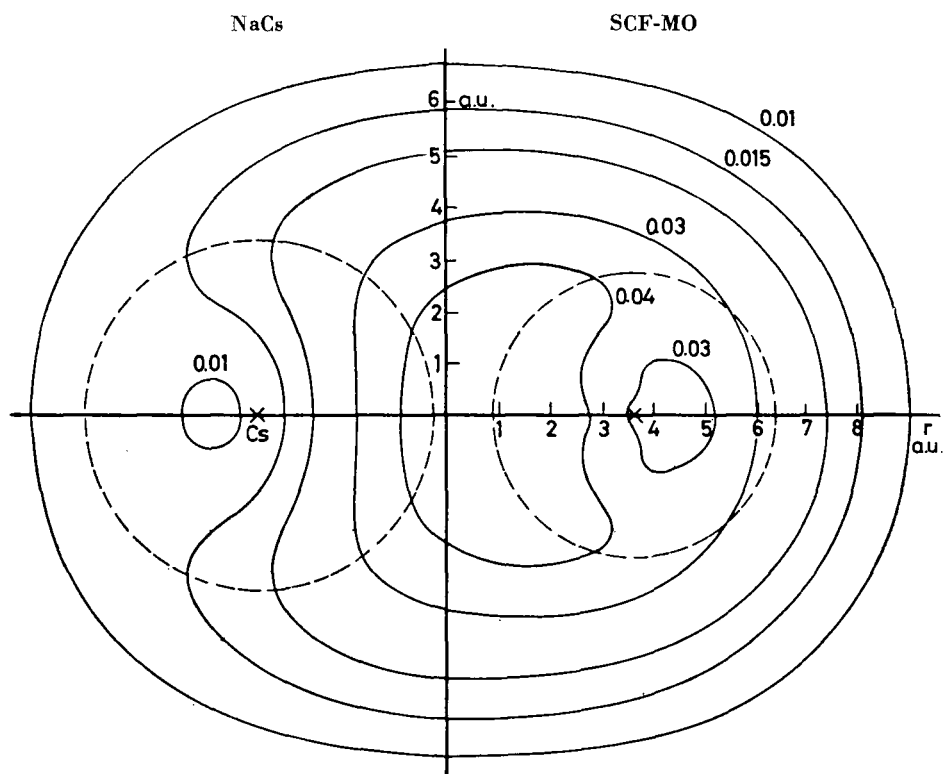


Fig. 5. Ground state SCF-MO for NaCs. The broken line indicates the core region. Inside this region the plots have no physical meaning

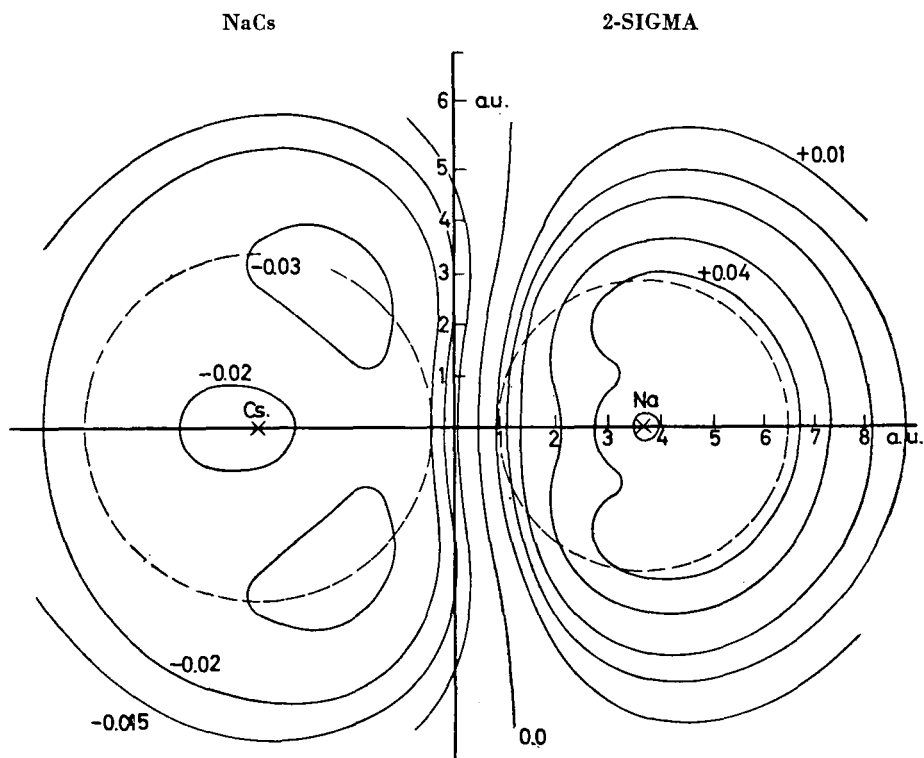


Fig. 6. 2σ -NO of NaCs with one node in the middle

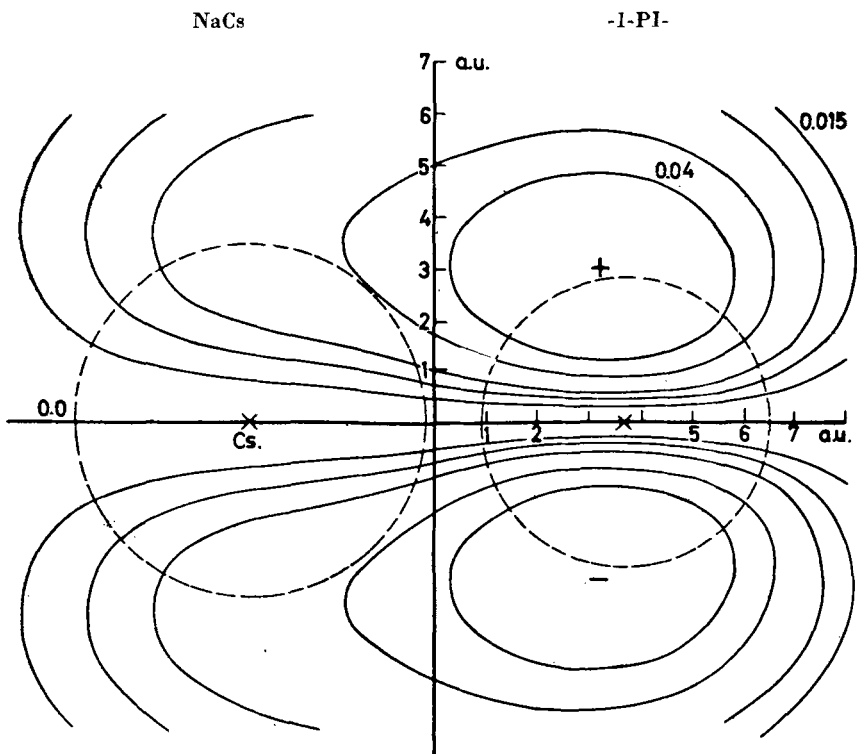


Fig. 7. 1π -NO of NaCs in the x - y -plane

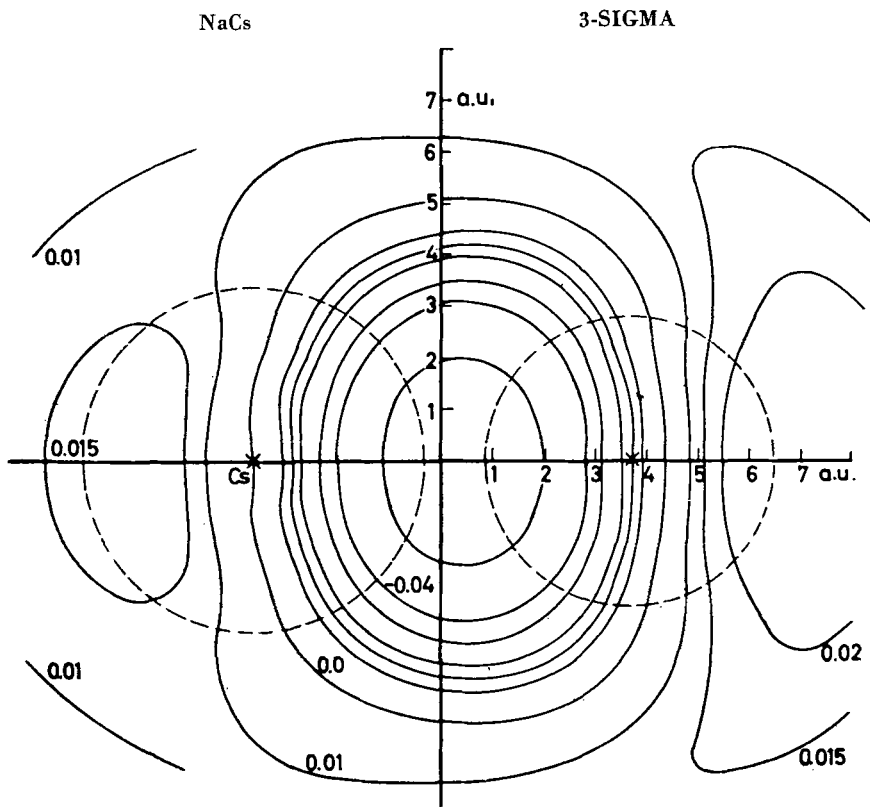


Fig. 8. 3σ -NO of NaCs with one node

Table VI

Comparison of BeH_2 in the pseudopotential scheme and a complete treatment.
All quantities are in atomic units

approx.	R_e	a_0	a_1	r_e	$-E_{HF}$	$-\varepsilon_{HF}$
pseudo- potential	1.356	-1.478	2.175	2.5	2.0558	$\varepsilon_1 = 0.5124$ $\varepsilon_2 = 0.4019$
complete SCF—NO				2.5	15.7624	$\varepsilon_1 = 0.4916$ $\varepsilon_2 = 0.4559$

approx.	$-E_{\text{corr}}^{\sigma}$	$-E_{\text{corr}}^{\pi}$	$-E_{\text{Tot.}}$	$-I_p$	D_e calc.	D_e estim.
pseudo- potential	0.0335	0.0230	2.11237	2.01184	0.1005	0.239
complete SCF—NO	0.0322	0.0245	15.8119		0.202	15.906

Conclusions

In performing molecular calculations in a pseudopotential approach one introduces two possible sources of errors. One is due to the approximation inherent in the chosen pseudopotential, the other to the limitations in the ansatz of wave functions. The latter source of error is the same as in all electron calculations and it is these errors which we tried to reduce as much as possible by aiming at a rather accurate treatment of the two and four valence-electron problem in the field of a pseudopotential that has a simple analytic form.

We performed Hartree—Fock calculations in the pseudopotential field and obtained good agreement with all-electron Hartree—Fock calculations (as far as those are available), both with respect to orbital energies and binding energies. Since Hartree—Fock calculations generally lead to good molecular geometries it is not surprising that the bond distances of our pseudopotential Hartree-Fock calculations agree well with the experimental ones.

The binding energies obtained in the Hartree—Fock approximation are as poor in a pseudopotential as in an all-electron treatment. In order to obtain the correct values one has to account for electron correlation. If one does so, by using the natural orbital expansion method one obtains about 60—80% of the experimental binding energies. (Whereas in the Hartree—Fock approach not even the sign of the binding energy is correct). In those cases where we could make the comparison, the correlation energies and the contributions of

the different NO's to it were quite similar in a pseudopotential and in an all-electron calculation. (This is demonstrated by the examples BeH_2 and Li_2 . For the larger systems the all-electron calculations would be much too time-consuming).

Two forms of the pseudopotential have been used, which differ appreciably inside the core region but which lead to rather similar results. A more careful inspection shows that the potential W^1 (see Fig. 1) is preferable to W^0 both with respect to Rydberg series and to binding energies.

Our results suggest that the pseudopotential method should be applicable successfully to larger molecules although some problems still remain. In particular we think that a strictly local potential is too poor for systems where the contributions of p -AO's to bonding is as important as that of s -AO's, so that for such systems either an l -dependent potential has to be used or one has to find a local potential that reproduces both s - and p -type Rydberg states if this is possible.

Appendix

If we write the pseudopotential in the form

$$\begin{aligned} -W_c^n(|\mathbf{r} - \mathbf{r}_c|) &= \sum_{\nu=0}^n a_\nu |\mathbf{r} - \mathbf{r}_c|^\nu & r < R \\ &= + \frac{Z_R}{|\mathbf{r} - \mathbf{r}_c|} & r > R \end{aligned} \quad (1)$$

the basis functions φ_μ as

$$\varphi_\mu = \left(\frac{2\alpha_\mu}{\pi} \right)^{3/4} e^{-\alpha_\mu(r-r_\mu)^2} \quad \mu = a, b, c, d, \dots \quad (2)$$

then we get in a first step with $\gamma = \alpha_a + \alpha_b$

$$-J = (\varphi_a, W_c^n \varphi_b) = \left(\frac{\alpha_a + \alpha_b}{\pi} \right)^{3/2} S_{ab} \int e^{-\gamma(r-r_p)^2} W_c^n(|\mathbf{r} - \mathbf{r}_c|) d\tau. \quad (3)$$

In this expression S_{ab} means the overlap integral (φ_a, φ_b) which is given by

$$\begin{aligned} S_{ab} &= (\alpha_a \cdot \alpha_b)^{-3/4} A^{3/2} e^{-1/2(\alpha_a - \alpha_b)^2 A}, \\ A &= \frac{2\alpha_a \cdot \alpha_b}{\alpha_a + \alpha_b}. \end{aligned} \quad (4)$$

Defining the position vector of the function centers or nucleus c by

$$\begin{aligned} \mathbf{a} &= [A_x; A_y; A_z], \\ \mathbf{b} &= [B_x; B_y; B_z], \\ \mathbf{c} &= [C_x; C_y; C_z] \end{aligned} \quad (5)$$

the point P with position vector \mathbf{r}_p in Equ. (3) is situated on the line between \mathbf{a} and \mathbf{b} with coordinates

$$\mathbf{r}_p = \frac{1}{\gamma} [\alpha_a A_x + \alpha_b B_x; \alpha_a A_y + \alpha_b B_y; \alpha_a A_z + \alpha_b B_z]. \quad (6)$$

Now we can transform our coordinates according to $\mathbf{r}' = \mathbf{r} - \mathbf{r}_c$ and get

$$-J = \left(\frac{\gamma}{2}\right)^{3/2} S_{ab} \int e^{-\gamma(r'-r_{cp})^2} W(|\mathbf{r}'|) d\mathbf{r}' \quad (7)$$

with $r_{cp} = r_c - r_p$.

Now we separate the integrations

$$-J = \left(\frac{\gamma}{\pi}\right)^{3/2} S_{ab} \left[\int_0^\infty e^{-\gamma(r^2+r_{cp}^2)} W(r) r^2 dr \int_{-1}^{+1} e^{2\gamma r_{cp} r x} dx \int_0^{2\pi} d\varphi \right] \quad (8)$$

and get after a short calculation

$$-J = \left(\frac{\gamma}{\pi}\right)^{3/2} S_{ab} \frac{\pi}{\gamma r_{cp}} \left[\int_0^\infty e^{-\gamma(r-r_{cp})^2} W(r) r dr - \int_0^\infty e^{-\gamma(r+r_{cp})^2} W(r) dr \right]. \quad (9)$$

Up to this point the derivation does not depend on the explicit potential expression from which we make use now.

$$\begin{aligned} J &= \left(\frac{\gamma}{\pi}\right)^{3/2} S_{ab} \frac{\pi}{\gamma r_{cp}} \left\{ \sum_{\nu=0}^n a_\nu \left[\int_0^R r^{\nu+1} e^{-\gamma(r-r_{cp})^2} dr - \int_0^R r^{\nu+1} e^{-\gamma(r+r_{cp})^2} dr \right] + \right. \\ &\quad \left. + Z_R \int_R^\infty e^{-\gamma(r-r_{cp})^2} dr - Z_R \int_R^\infty e^{-\gamma(r+r_{cp})^2} dr \right\}. \end{aligned} \quad (10)$$

After substitution

$$u = r - r_{cp}, \quad v = r + r_{cp}$$

we get for $r^{\nu+1}$ an expression

$$(u + r_{cp})^{\nu+1} = \sum_{\lambda=0}^{\nu+1} \binom{\nu+1}{\lambda} u^\lambda r_{cp}^{\nu-\lambda+1} \quad (11)$$

and the corresponding one for $(v-r_{cp})^{\nu+1}$. Therefore we can write for the whole integral

$$J = \left(\frac{\gamma}{\pi}\right)^{3/2} S_{ab} \left\{ \frac{\pi}{\gamma} \sum_{\nu=0}^n a_{\nu} \sum_{\lambda=0}^{\nu+1} \binom{\nu+1}{\lambda} r_{cp}^{\nu-\lambda} \left[\int_{-r_{cp}}^{R-r_{cp}} u^{\lambda} e^{-\gamma u^2} du + (-1)^{\nu-\lambda} \int_{r_{cp}}^{R+r_{cp}} v^{\lambda} e^{-\gamma v^2} dv \right] + \frac{Z_R \pi}{\gamma r_{cp}} \left[\int_{R-r_{cp}}^{\infty} e^{-\gamma u^2} du - \int_{R+r_{cp}}^{\infty} e^{-\gamma u^2} du \right] \right\}. \tag{12}$$

After some simplifications in the last two integrals and a splitting of the first term in the sum over ν we obtain the final form

$$J = \sqrt{\frac{\gamma}{\pi}} S_{ab} \left\{ \frac{a_0}{2} \sqrt{\frac{\pi}{\gamma}} [\operatorname{erf}(\sqrt{\gamma}(r_{cp} + R)) - \operatorname{erf}(\sqrt{\gamma}(r_{cp} - R))] + \frac{Z_R}{2 r_{cp}} \sqrt{\frac{\pi}{\gamma}} [\operatorname{erf}(\sqrt{\gamma}(r_{cp} + R)) + \operatorname{erf}(\sqrt{\gamma}(r_{cp} - R))] + \frac{a_0}{2\gamma r_{cp}} [e^{-\gamma(r_{cp}+R)^2} - e^{-\gamma(r_{cp}-R)^2}] + \sum_{\nu=1}^n a_{\nu} \left[\frac{r_{cp}^{\nu}}{\sqrt{\gamma}} \left(\int_{-\sqrt{\gamma}r_{cp}}^{\sqrt{\gamma}(R-r_{cp})^2} e^{-u^2} du + (-1)^{\nu} \int_{\sqrt{\gamma}r_{cp}}^{\sqrt{\gamma}(R+r_{cp})^2} e^{-u^2} du \right) + \sum_{\lambda=1}^{\nu+1} \binom{\nu+1}{\lambda} r_{cp}^{\nu-\lambda} \sqrt{\gamma}^{-\lambda-1} \left(\int_{-\sqrt{\gamma}r_{cp}}^{\sqrt{\gamma}(R-r_{cp})^2} u^{\lambda} e^{-u^2} du + (-1)^{\nu-\lambda} \int_{\sqrt{\gamma}r_{cp}}^{\sqrt{\gamma}(R+r_{cp})^2} u^{\lambda} e^{-u^2} du \right) \right] \right\}. \tag{13}$$

In this expression the terms with $\nu = 0$ and $\lambda = 0$ are written down separately because they can be reduced to simple analytic expressions. So II can be written as

$$II = \sqrt{\frac{\pi}{4}} [(1 - (-1)^{\nu}) \operatorname{erf}(\sqrt{\gamma}r_{cp}) + \operatorname{erf}(\sqrt{\gamma}(R-r_{cp})) + (-1)^{\nu} \operatorname{erf}(\sqrt{\gamma}(R+r_{cp}))] \tag{14}$$

with
$$\operatorname{erf}(z) = \frac{2}{\sqrt{\gamma}} \int_0^z e^{-u^2} du. \tag{15}$$

The remaining integrals which are of the form

$$J_{\lambda}(a, b) = \int_a^b u^{\lambda} e^{-u^2} du \tag{16}$$

can easily be evaluated by a recurring relation one can derive from
$$J_{\lambda}(a, b) = \frac{1}{2} [(\lambda-2)J_{\lambda-2}(a, b) + a^{\lambda-2} e^{-a^2} - b^{\lambda-2} e^{-b^2}] \tag{17}$$

which connects $J_\lambda(a, b)$ with $J_{\lambda-2}(a, b)$.

The initial integrals $J_1(a, b)$ and $J_2(a, b)$ are

$$J_1(a, b) = \frac{1}{2} \sqrt{\pi} [\operatorname{erf}(b) - \operatorname{erf}(a)],$$

$$J_2(a, b) = \frac{1}{2} [e^{-a^2} - e^{-b^2}]$$

so that the whole integral ($\varphi_a, W_c \varphi_b$) is reduced to the evaluation of the error-function.

For practical calculations it is useful to introduce some approximations for the limiting case $r_{cp} \ll 1$, to avoid numerical instabilities.

In this case we have approximated the expressions for I and II by

$$\begin{aligned} \text{I} &= \frac{r_{cp}^{\nu-\lambda}}{\sqrt{\gamma}^{\lambda+1}} \left(\int_{-\sqrt{\gamma} r_{cp}}^{\sqrt{\gamma}(R-r_{cp})} u^\lambda e^{-u^2} du + (-1)^{\nu-\lambda} \int_{\sqrt{\gamma} r_{cp}}^{\sqrt{\gamma}(R+r_{cp})} u^\lambda e^{-u^2} du \right) \approx \\ &\approx \frac{1}{\sqrt{\gamma}^{\nu+1}} \left[(1 + (-1)^{\nu-\lambda}) (\sqrt{\gamma} r_{cp})^{\nu-\lambda} \int_0^{\sqrt{\gamma} R} u^\lambda e^{-u^2} du - \right. \\ &\quad \left. - (\sqrt{\gamma} r_{cp})^{\nu+1-\lambda} (\sqrt{\gamma} R)^\lambda e^{-\gamma R^2} (1 - (-1)^{\nu-\lambda}) \right] \\ \text{II} &\approx \frac{\sqrt{\pi}}{2} (1 + (-1)^\nu) \operatorname{erf}(\sqrt{\gamma} R) + (1 - (-1)^\nu) \sqrt{\gamma} r_{cp} (1 - e^{\gamma R^2}). \end{aligned}$$

Acknowledgement

The research reported here has been sponsored in part by "Deutsche Forschungsgemeinschaft" and "Fond der chemischen Industrie". Several subroutines used are due to Dr. R. AHLRICHS to whom the authors are also indebted for stimulating discussions. Thanks are also due to various colleagues (C. K. JÖRGENSEN and G. KLOPMAN formerly in Geneva, W. H. E. SCHWARZ, formerly in Frankfurt and the audience of the Theoretical Chemistry Symposium 1968 in Elmau) for discussions following talks by two of the authors (R.-J. K. and W. K.) on this subject.

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ПОДРАЖЕНИЕ ВЛИЯНИЯ ЭЛЕКТРОНОВ АТОМНОГО ОСТАТКА ПСЕВДОПОТЕНЦИАЛАМ. II.

ПРИМЕНЕНИЯ К НЕКОТОРЫМ МОЛЕКУЛАМ С ДВУМЯ И ТРЕМЯ АТОМАМИ

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Резюме

Псевдопотенциальная теория комбинируется с методом Хартри—Фока и методом естественного разложения в ряд с целью определения молекулярных постоянных D_e , R_e и k_e для Na_2 , K_2 , NaCs и BeH_2 . Эти молекулы рассматривались как двух- и четырех-электронные проблемы соответственно в псевдопотенциальном поле своих атомных остатков. Далее были анализированы энергии и волновые функции с точки зрения вноса различных натуральных орбит в корреляционную энергию. Вычисленные расстояния равновесия хорошо согласуются с экспериментальными данными. Соответствие диссоциационных энергий с экспериментальными данными лучше, чем в предыдущих вычислениях.