Theoret. chim. Acta (Berl.) 9, 324—329 (1968)

Relationes

Simple Accurate Two-Centre Wave-Functions for Homonuclear Diatomic Molecules

M. Cohen*, Brenda H. Dorrell, and R. P. McEachran

Centre for Research in Experimental Space Science and Department of Physics,
York University, Toronto, Canada

Received August 1, 1967

1. Introduction

Two-centre approximate molecular orbitals, based on the simple "united-atom" approximation and including a variational charge parameter, have been calculated for the lowest even and odd σ, π and δ states of homonuclear diatomic molecule ions of arbitrary nuclear charge Z. These approximate electronic wave-functions are shown to satisfy the same scaling equations with respect to Z as the exact solutions. They are very accurate at small internuclear separations for all states, but at larger separations there is some loss of accuracy which can be compensated by including corrections calculated by conventional Rayleigh-Schrödinger perturbation theory.

Theoretical investigations of the electronic structure and the physical and chemical properties of many electron atoms have relied heavily on the well-known solutions of the Schrödinger equation for the hydrogen atom and its isoelectronic ions. Indeed, remarkably accurate predictions have often been made on the basis of very simple "screened" hydrogen-like orbitals or (nodeless) Slater orbitals (Morse, Young, and Haurwitz [7]; Bolotin, Levinson, and Levin [1]).

Calculations on homonuclear diatomic molecules should in principle begin with the corresponding solutions of the Schrödinger equation for the hydrogen molecule-ion and ions isoelectronic with it. Effectively *exact* solutions of the H_2^+ problem for a large number of states have been calculated by many authors, the most recent tabulation being that of Hunter and Pritchard [6]. These "exact" solutions are too complicated to be used in calculations on larger systems, and simple approximations to them are desirable.

We have recently investigated the accuracy of a two-centre approximation in which simple "united atom" wave functions are improved by means of conventional Rayleigh-Schrödinger perturbation theory to yield accurate solutions for a number of states of H_2^+ (Cohen, and McEachran [2]; Cohen, Dorrell, and McEachran [3]; and Cohen, McEachran, and McPhee [4]). We shall now show that our approximation procedures are readily extended to the treatment of systems having arbitrary nuclear charge, and the resulting wave-functions should therefore serve as useful approximations to molecular orbitals in many-electron homonuclear systems.

---

* Present address: Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel.

2. Scaling Relations and Exact Solutions for Arbitrary Nuclear Charge Z

The non-relativistic Schrödinger equation which describes the motion of a single electron moving in the joint Coulomb field of two nuclei each of charge Z atomic units (a. u.) which are supposed fixed at a separation of 2 R a.u. may be written conveniently as

$$H(Z, R)\,\Psi(Z, R) = E(Z, R)\,\Psi(Z, R)\,. \tag{1}$$

In the notation of Fig. 1, the *electronic* Hamiltonian $H(Z, R)$ may be written in atomic units

$$H(Z, R) = -\tfrac{1}{2}\nabla^2 - Z\left(\frac{1}{r_a} + \frac{1}{r_b}\right) \tag{2}$$

or, more conveniently, in confocal elliptic coordinates (which take explicit account of the molecular geometry)

$$H(Z, R) = -\frac{1}{2R^2(\lambda^2-\mu^2)} \times\left\{\frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial}{\partial\lambda}\right] + \frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial}{\partial\mu}\right] + \frac{(\lambda^2-\mu^2)}{(\lambda^2-1)(1-\mu^2)}\frac{\partial^2}{\partial\varphi^2} + 4ZR\lambda\right\}. \tag{3}$$

In this coordinate system, φ is the azimuthal angle measured about the internuclear axis (conveniently chosen as z-axis), while λ and μ are defined by the relations

$$\lambda = \frac{r_a + r_b}{2R}\,, \qquad \mu = \frac{r_a - r_b}{2R} \tag{4}$$

so that

$$1 \leq \lambda < \infty\,, \quad -1 \leq \mu \leq 1\,, \quad 0 \leq \varphi < 2\pi\,. \tag{5}$$

If all distances are now scaled according to

$$\bar{r}_a = Zr_a\,, \quad \bar{r}_b = Zr_b\,, \quad \bar{R} = ZR \tag{6}$$

we find that λ, μ and φ are all unchanged, so that we have from (3)

$$H(Z, R) = Z^2 H(1, \bar{R}) \equiv Z^2 H(1, ZR)\,. \tag{7}$$

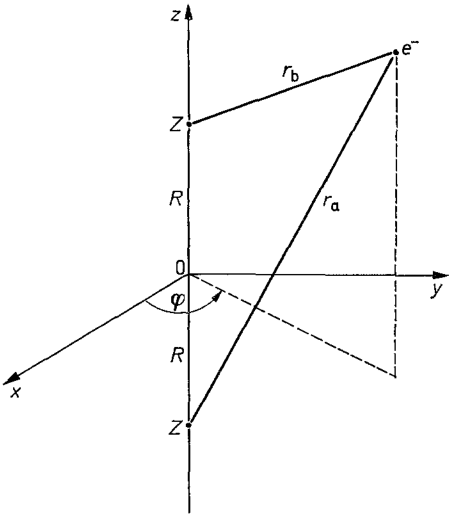

Fig. 1

Similarly we may deduce from (1) the *scaling equations* for the energy eigenvalues

$$E(Z, R) = Z^2 E(1, \bar{R}) \equiv Z^2 E(1, ZR) , \tag{8}$$

and for the *unnormalized* eigenfunctions

$$\Psi(Z, R) = \Psi(1, \bar{R}) \equiv \Psi(1, ZR) . \tag{9}$$

Thus knowledge of the exact solutions for $Z = 1$ at a given internuclear separation R suffices to give the corresponding solutions for *any* Z at a separation R/Z.

Our approximate solutions will now be shown to satisfy the same scaling Eqs. [(8) and (9) above] as the exact solutions. For simplicity of presentation, we treat in detail the case of the $1s\sigma_g$ (ground) state, but the argument is easily generalized to other states. As far as possible, we follow the notations of Cohen and McEachran [2].

3. Scaling of the Approximate Solution for the $1s\sigma_g$-State

We choose the unnormalized "united-atom" approximation

$$\Psi_0(\alpha; Z, R) = \exp(-\alpha R \lambda) = \exp(-p\lambda) , \tag{10}$$

say, where $\alpha(Z, R)$ is a disposable "charge" parameter. This $\Psi_0(\alpha; Z, R)$ satisfies the zero-order Schrödinger equation

$$[H_0(\alpha; Z, R) - E_0(\alpha; Z, R)] \Psi_0(\alpha; Z, R) = 0 , \tag{11}$$

and we may choose for convenience $E_0(\alpha; Z, R) = -\frac{1}{2}\alpha^2$.

The effective Hamiltonian $H_0(\alpha; Z, R)$ is then defined in terms of the electronic Hamiltonian $H(Z, R)$ of Eq. (3) and the "perturbation operator" $H_1(\alpha; Z, R)$ by means of

$$H_0(\alpha; Z, R) = H(Z, R) - H_1(\alpha; Z, R) . \tag{12}$$

Explicitly, we have

$$H_1(\alpha; Z, R) = \frac{1}{2R^2(\lambda^2 - \mu^2)} \{2 R(\alpha - 2 Z) \lambda + \alpha^2 R^2(1 - \mu^2)\} \tag{13}$$

and

$$\begin{aligned} E_1 &= \langle \Psi_0 \,|\, H_1 \,|\, \Psi_0 \rangle / \langle \Psi_0 \,|\, \Psi_0 \rangle \\ &= \frac{\alpha^2 (1 + 2\alpha R + \frac{2}{3} \alpha^2 R^2) - 2Z\alpha (1 + 2\alpha R)}{1 + 2\alpha R + \frac{3}{4} \alpha^2 R^2} . \end{aligned} \tag{14}$$

The charge parameter $\alpha(Z, R)$ is now determined by optimizing the total energy through first order. This procedure leads in this case to the algebraic equation:

$$4 p^4 + 12 p^3 + (12 - 16 \bar{R}) p^2 + (3 - 24 \bar{R}) p - 6 \bar{R} = 0 . \tag{15}$$

Clearly, solutions of (15) must be of the form $p = p(1, \bar{R})$, so that

$$\alpha(Z, R) = Zp(1, \bar{R})/\bar{R} = Z\bar{\alpha}(1, ZR) , \tag{16}$$

say. We now have from (10) and (14),

$$E_0(\alpha; Z, R) = Z^2 E_0(\bar{\alpha}; 1, \bar{R}) , \qquad \Psi_0(\alpha; Z, R) = \Psi_0(\bar{\alpha}; 1, \bar{R}) \tag{17}$$

$$E_1(\alpha; Z, R) = Z^2 E_1(\bar{\alpha}; 1, \bar{R}) \tag{18}$$

and from (13)

$$H_1(\alpha; Z, R) = Z^2 H_1(\bar{\alpha}; 1, \bar{R}). \tag{19}$$

Since both $H(Z, R)$ and $H_1(\alpha; Z, R)$ scale in the same way, we deduce that

$$H_0(\alpha; Z, R) = Z^2 H_0(\bar{\alpha}; 1, \bar{R}) \tag{20}$$

and we may now prove inductively that

$$\Psi_n(\alpha; Z, R) = \Psi_n(\bar{\alpha}; 1, \bar{R}) \tag{21a}$$

and

$$E_n(\alpha; Z, R) = Z^2 E_n(\bar{\alpha}; 1, \bar{R}) \tag{21b}$$

for *every* term in the perturbation expansions

$$\Psi(Z, R) = \sum_{n=0}^{\infty} \Psi_n(\alpha; Z, R) \tag{22a}$$

and

$$E(Z, R) = \sum_{n=0}^{\infty} E_n(\alpha; Z, R). \tag{22b}$$

Thus, our approximate solutions (which are all based on the "united-atom" approximation and refined by means of Rayleigh-Schrödinger perturbation theory) may be shown to satisfy the *exact* scaling Eqs. (8) and (9). Further, *each term* in the perturbation expansions [Eq. (22) above] scales correctly, so that our earlier results for H_2^+ ($Z = 1$) are easily adapted to systems with arbitrary nuclear charge Z.

4. Discussion

Zero-Order Solutions

The zero-order "united atom" solutions $\Psi_0(\alpha; Z, R)$, where α is the "effective charge" parameter, are selected according to the prescription of DALGARNO and LEWIS [5]. However, it is actually more convenient to present values of the "screening" parameter s which is related to α by means of

$$\alpha(Z, R) = \frac{2}{n}[Z - s(Z, R)] \tag{23}$$

where n is the principal quantum number of the state considered. It is clear that s scales in the same way as α, so that

$$s(Z, R) = Zs(1, \bar{R}) \equiv Zs(1, ZR). \tag{24}$$

The table contains our calculated values of these "reduced" screening parameters, $s(1, ZR)$, tabulated over the range of ZR values from 0 to 4. Intermediate values can be interpolated with confidence from our tabulated entries, since our own calculations indicate that the energies are quite insensitive to small changes in the last two decimal places. It is interesting to note that the screening parameters are all positive for the bonding states ($1s\sigma_g$, $2p\pi_u$, $3d\delta_g$) and all negative for the corresponding antibonding states ($2p\sigma_u$, $3d\pi_g$, $4f\delta_u$).

First-Order Solutions

The first-order Rayleigh-Schrödinger perturbation equation can be solved exactly for $\Psi_1(\alpha; Z, R)$ by the methods of COHEN and MCEACHRAN [2]. The scaling

Table. *Reduced screening parameters*, $s\,(1, ZR)$

ZR	State					
	$1s\sigma_g$	$2p\sigma_u$	$2p\pi_u$	$3d\pi_g$	$3d\delta_g$	$4f\delta_u$
0.125	0.04291	−0.01334	0.00401	−0.00086	0.00079	−0.00009
0.250	0.10427	−0.05183	0.01468	−0.00337	0.00311	−0.00037
0.375	0.15880	−0.11164	0.02962	−0.00742	0.00683	−0.00082
0.500	0.20502	−0.18484	0.04686	−0.01279	0.01178	−0.00143
0.625	0.24428	−0.25856	0.06509	−0.01923	0.01775	−0.00219
0.750	0.27801	−0.32055	0.08350	−0.02646	0.02455	−0.00307
0.875	0.30735	−0.36511	0.10164	−0.03417	0.03199	−0.00406
1.000	0.33316	−0.39287	0.11924	−0.04207	0.03991	−0.00512
1.125	0.35609	−0.40713	0.13617	−0.04987	0.04817	−0.00623
1.250	0.37666	−0.41145	0.15237	−0.05731	0.05667	−0.00736
1.375	0.39523	−0.40874	0.16784	−0.06418	0.06530	−0.00849
1.500	0.41213	−0.40119	0.18258	−0.07032	0.07400	−0.00960
1.625	0.42758	−0.39035	0.19663	−0.07562	0.08271	−0.01065
1.750	0.44179	−0.37731	0.21000	−0.08001	0.09138	−0.01162
1.875	0.45493	−0.36287	0.22275	−0.08346	0.09998	−0.01250
2.000	0.46711	−0.34756	0.23491	−0.08597	0.10848	−0.01327
2.250	0.48907	−0.31577	0.25761	−0.08836	0.12509	−0.01442
2.500	0.50836	−0.28386	0.27836	−0.08761	0.14112	−0.01496
2.750	0.52549	−0.25277	0.29741	−0.08427	0.15651	−0.01485
3.000	0.54085	−0.22295	0.31498	−0.07888	0.17126	−0.01407
3.250	0.55472	−0.19458	0.33123	−0.07190	0.18536	−0.01263
3.500	0.56734	−0.16771	0.34633	−0.06375	0.19884	−0.01056
3.750	0.57888	−0.14230	0.36039	−0.05473	0.21172	−0.00790
4.000	0.58951	−0.11829	0.37354	−0.04512	0.22402	−0.00471

of our first-order solutions has been described above. The improvement in the energy values calculated using the first-order approximation

$$\Psi(\alpha; Z, R) = \Psi_0(\alpha; Z, R) + \Psi_1(\alpha; Z, R) \tag{25}$$

is significant, the more so at the larger separations, and particularly for σ states.

The accuracy at larger values of ZR may be improved further by introducing the *linear* variation parameter η into the approximate solution

$$\Psi(\alpha, \eta; Z, R) = \Psi_0(\alpha; Z, R) + \eta\, \Psi_1(\alpha; Z, R)\,. \tag{26}$$

The values of η are *independent* of Z; this is a consequence of the fact that Ψ_0 and Ψ_1 both scale in the same way as the exact Ψ.

Molecular properties other than the electronic energy can easily be deduced from the data on H_2^+ by scaling procedures similar to those described above. The accuracy of our earlier calculations [2, 3, 4] will thus carry over to systems with arbitrary Z, so that the approximate wavefunctions may be regarded as sufficiently accurate for many purposes.

It seems likely that the simple united-atom (zero order) solutions will provide adequate descriptions of the electronic properties of π and δ orbitals of many-electron molecules. For the σ orbitals, our first-order solutions should serve as satisfactory approximations.

Acknowledgments. The computations described here were performed on the IBM 7094 computer of the University of Toronto and the IBM 360 computer of York University. The research reported has been supported in part by the National Research Council of Canada, by the Defence Research Board of Canada under grant No. 9510-49 and by the Air Force Cambridge Research Centre under contract No. AF 19(628)-5813.

References

1. Bolotin, A. B., I. B. Levinson, and L. I. Levin: Sov. Physics **2**, 391 (1956).
2. Cohen, M., and R. P. McEachran: Can. J. Physics **44**, 2809 (1966).
3. —, B. H. Dorrell, and R. P. McEachran: Can. J. Physics **44**, 2827 (1966).
4. —, R. P. McEachran, and S. D. McPhee: Can. J. Physics **45**, 2533 (1967).
5. Dalgarno, A., and J. T. Lewis: Proc. physic. Soc. [London] **A69**, 285 (1956).
6. Hunter, G., and H. O. Pritchard: J. chem. Physics **46**, 2146 (1967).
7. Morse, P. M., L. A. Young, and E. S. Haurwitz: Physic. Rev. **48**, 948 (1935).

Professor R. P. McEachran
Centre for Research in
Experimental Space Science
York University
Toronto 12, Ontario, Canada