

# The Elements of Flatland: Hartree-Fock Atomic Ground States in Two Dimensions for $Z = 1-24$

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## Abstract

The Hartree-Fock problem in two dimensions (2D) has been solved for  $1 \leq Z \leq 24$  using a Gaussian basis and assuming  $r^{-1}$  Coulomb interactions. The order of occupation of the one-electron states is

$$1s \ll 2s < 2p < 3s < 3p < 4s \approx 3d < 4p,$$

like in the 3D case. The  $1s$  shell is found to be particularly small and strongly bound, making the 2D hydrogen a "superhalogen" and the 2D He a "superinert gas." In contrast to 3D,  $4s^1 3d^2$  and  $4s^2 3d^3$  configurations are preferred for the 2D "Sc" and "Cu," respectively. The six first 2D atoms have stronger and the later ones weaker valence-bonding energies than do their 3D analogs. It is noted that the 2D Dirac energy expression for a hydrogenlike atom for  $m_j = l + 1/2$  agrees with the 3D Klein-Gordon one.

## 1. Introduction

In an international chemistry contest for teen-agers, the participants were recently asked to construct the periodic system for a two-dimensional (2D) world. The correct answer, by analogy to the 3D case, was supposed to be that in Figure 1 [1]. We provide here an answer, at the Hartree-Fock level, to what the actual filling order would be for the 24 first elements assuming  $r^{-1}$  Coulomb interactions between the particles.

The problem is actually of genuine scientific interest: The trends [2] in the usual periodic system (Fig. 2) all occur also in the 2D case, but their proportions could vary. Thus, instead of just one object to study, we would at least have two.

The 2D one-particle problem has been used as a model for strongly anisotropic semiconductors [3, 4] and also as a limiting case for H-like atoms in high magnetic fields [5]. For  $D$ -dimensional H and  $H_2^+$  ( $D = 2-100$ ), see Frantz and Herschbach [6] and references therein. The 2D two-electron problem was studied by de Andrada e Silva et al. [7] and Fabbri and da Silva [8] on He and  $H_2$ . More generally, the  $D$ -dimensional two-electron atoms were solved with high accuracy by Loeser and Herschbach [9]. The many-electron atoms were discussed using a  $1/D$  expansion by Loeser [10].

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SOLUTIONS

Theoretical task 1

a) The Flatlandian periodic table:

1 $1s^1$							2 $1s^2$		
3 $12s^1$	4 $12s^2$					5 $12s^2 1p$	6 $12s^2 2p$	7 $12s^2 3p$	8 $12s^2 4p$
9 $13s^1$	10 $13s^2$					11 $13s^2 1p$	12 $13s^2 2p$	13 $13s^2 3p$	14 $13s^2 4p$
15 $14s^1$	16 $14s^2$	17 $14s^2 3d^1$	18 $14s^2 3d^2$	19 $14s^2 3d^3$	20 $14s^2 3d^4$	21 $14s^2 3d^4 1p$	22 $14s^2 3d^4 2p$	23 $14s^2 3d^4 3p$	24 $14s^2 3d^4 4p$

Figure 1. The suggested form of the 2D periodic system by Laitinen and Pakkanen [1].

2. The One-Electron Case

2.1. Nonrelativistic Case

The 2D Kepler problem was solved analytically by Jauch and Hill [11] for the bound states and by Shinada and Sugano [4] for the continuum. For later discussions, see MacDonald and Ritchie [5]. To emphasize the analogy with the 3D case, we label the  $(n + 1/2)l$  states  $1s, 2s, 2p, 3s, 3p, 3d, \dots$ , where  $n$  is the half-integer and the orbital angular momentum is  $\pm \hbar l$ . Then, the eigenvalues (in a.u.,  $e = \hbar = m_e = 4\pi\epsilon_0 = 1$ ) become

$$E_{nl} = -(1/2) (Z/n)^2 \tag{2.1}$$

with

$$n = 1/2, 3/2, 5/2, \dots$$

$$l = |m_l|$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm(n - 1/2). \tag{2.2}$$

Thus, the  $n + 1/2 = 1, 2, 3, 4, \dots$  levels are  $2-, 6-, 10-, 14-, \dots$  fold degenerate, including, ad hoc, the spin, as contrasted to  $2-, 8-, 18-, 32-, \dots$  for 3D.

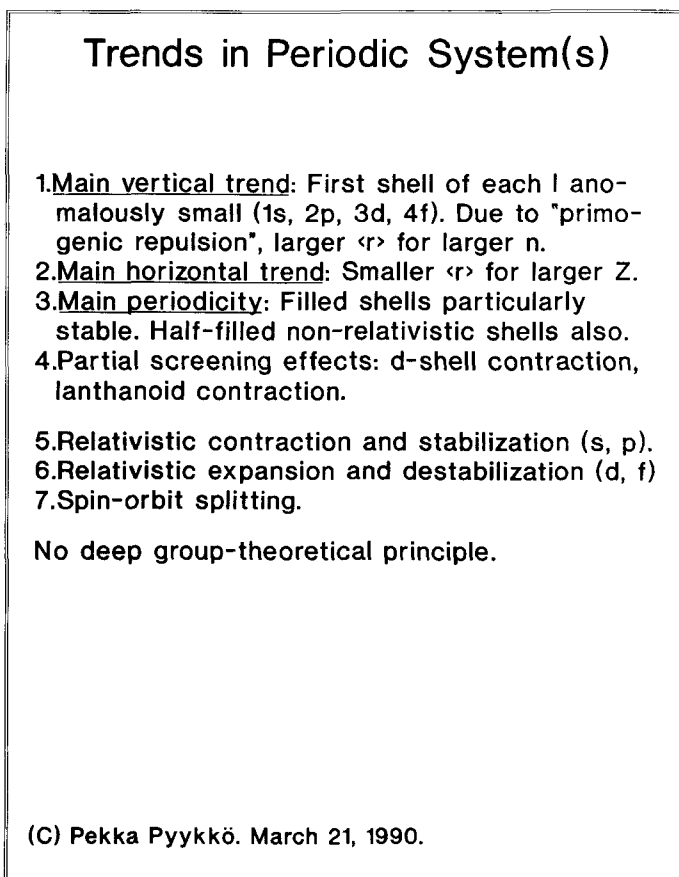


Figure 2. Trends in periodic systems (Pyykkö [2]).

The striking difference between the 3D and 2D cases is the very low-lying 1s state of the latter,  $E = -1/2$  and  $-2$  a.u., respectively ( $Z = 1$ ) (see Fig. 3). Otherwise, this spectrum suggests that the first  $d$ -shell ( $l = 2$ ) indeed would be occupied after the  $3s$  and  $3p$  ones, allowing for partial-screening effects.

The problem of  $D$ -dimensional hydrogen was considered by Moss [12]. From his paper we note that the eigenvalue ratio of the two lowest  $s$ -states becomes  $9, 4, 25/9 = 2.78, \dots$  for 2D, 3D, 4D,  $\dots$ . Thus, low  $D$  will place the 1s state deeper, in a relative scale.

## 2.2. Relativistic Case

The 2D Dirac hydrogen atom was considered by Coulson and Joseph [13], by Cížek and Paldus [14], and by Bruce [15] (see also Moss [12] and Sokalski [16]). The exact eigenvalues (in a.u.) become

$$E = c^2 \{ 1 + (Z/c)^2 [n - |m| + |m| (1 - (Z/c|m|)^2)^{1/2}]^{-2} \}^{-1/2}, \quad (2.3)$$

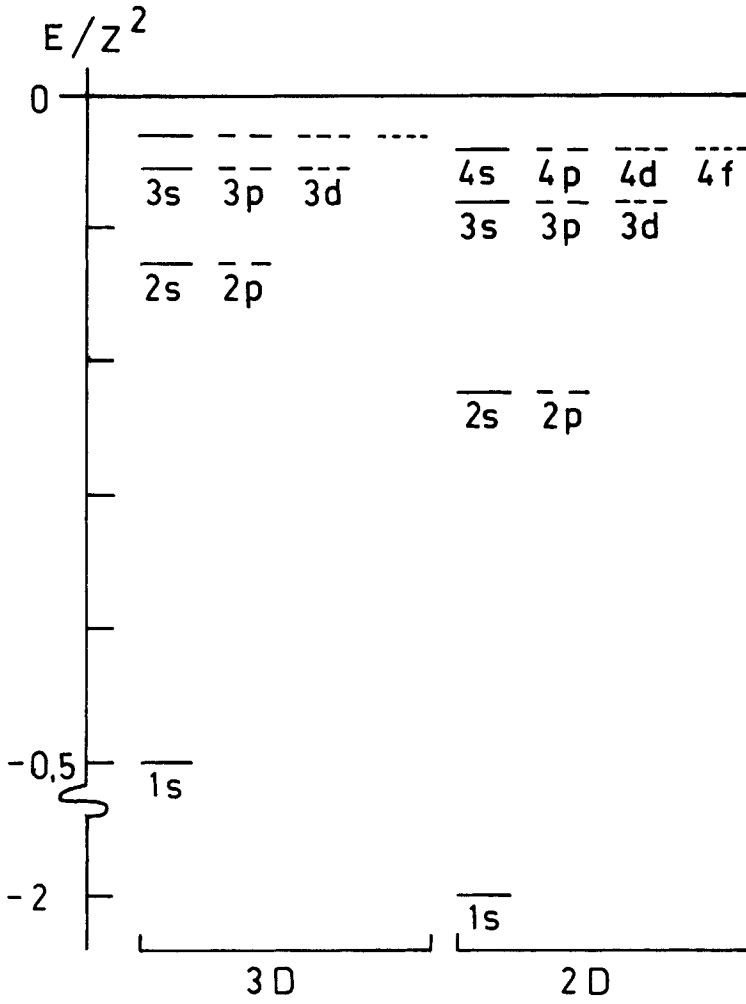


Figure 3. The nonrelativistic eigenvalue spectra of 3D and 2D hydrogen atoms.

where

$$\begin{aligned}
 m &\equiv m_j = m_l \pm 1/2 \\
 &= \pm 1/2, \pm 3/2, \pm 5/2, \dots
 \end{aligned}
 \tag{2.4}$$

For  $Z/c \rightarrow 0$ ,

$$E_{nm} = c^2 - (1/2)(Z/n)^2 + (1/2)(Z/n)^4 c^{-2} (3/4 - n/|m|) + \dots
 \tag{2.5}$$

We note that the 2D hydrogen 1s binding energy is

$$E_{1s} = -2 - 2/c^2 + 0(c^{-4}),
 \tag{2.6}$$

as is the 3D  $\text{He}^+$  one.

The expression (2.3) is defined for  $s$  or  $p_{1/2}$  states ( $|m| = 1/2$ ) up to  $Z/c = 1/2$ . In other words, only the  $137/2 = 68$  first elements have solutions for point nuclei. This situation is similar to the solution of the Klein–Gordon (K–G) equation for a Coulomb field [17]. In fact, the K–G 3D eigenvalues are identical with the Dirac 2D ones [Eq. (2.3)], for the larger  $m$  value of  $l + 1/2$ , including  $s_{1/2}$ . (The expressions are the same; the  $n$ -values are integer and half-integer, respectively.)

Sokalski [16] suggests that the  $m_s = \pm 1/2$  states of 2D Dirac electrons would actually be separated by  $2mc^2$  and that they would obey Bose–Einstein statistics and have no magnetic moment, unlike in the Pauli case.

### 3. The Many-electron Case

#### 3.1. Closed Shell

The Hamiltonian of the system is

$$H = \sum h_i + \sum g_{ij} \tag{3.1}$$

$$h_i = -(1/2)\nabla_i^2 - Z/r_i \tag{3.2}$$

$$g_{ij} = 1/r_{ij} \tag{3.3}$$

$$\nabla_i^2 = r^{-1}\partial/\partial r(r\partial/\partial r) + r^{-2}\partial^2/\partial\phi^2. \tag{3.4}$$

To keep the parallelism to the 3D case, we thus assume  $r^{-1}$  electron–electron and electron–nucleus interactions, despite the fact that the Poisson equation in the 2D case would require  $\ln r$  interactions [18].

In the closed-shell single-determinant case, the total energy

$$E = \langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle, \tag{3.5}$$

$$= |\phi_1\bar{\phi}_1 \dots \phi_n\bar{\phi}_n|, \tag{3.6}$$

becomes

$$E = 2 \sum_{i=1}^N I_i + \sum_{i,j=1}^N (2J_{ij} - K_{ij}), \tag{3.7}$$

with

$$I_i = \int \phi_i^*(1)h_i\phi_i(1) dv_i \tag{3.8}$$

$$J_{ij} = \int \phi_i^*(1)\phi_j^*(2)g_{12}\phi_i(1)\phi_j(2) dv_1 dv_2 \tag{3.9}$$

$$K_{ij} = \int \phi_i^*(1)\phi_j^*(2)g_{12}\phi_j(1)\phi_i(2) dv_1 dv_2. \tag{3.10}$$

We then classify the one-electron states  $i$  by the principal quantum number ( $n + 1/2$ ) and the angular momentum,  $m_i$ . For the absolute value  $l = |m_i|$ , we

use the symbols

$$\begin{aligned} \text{Symbol: } & s \quad p \quad d \quad f \quad g \quad h \dots \\ l: & 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \dots \end{aligned} \quad (3.11)$$

These one-electron states,

$$\phi_i(\mathbf{r}) = \phi_{nm_i}(\mathbf{r}) = R_{nl}(r) \exp(im_l \phi), \quad (3.12)$$

are then expanded in terms of the  $N_l$  Cartesian Gaussian functions:

$$\phi_{nm_i} = \sum_{i=1}^{N_l} C_{nm_i} \chi_{m_i}. \quad (3.13)$$

These basis functions are defined in Table I. The coefficients,  $C$ , are real. Introducing the density matrices

$$D_{m_p q} = 2 \sum_{n \in m_l}^{occ} C_{nm_i p} C_{nm_i q}, \quad (3.14)$$

the one-electron integrals

$$H_{m_p q} = \int \chi_{m_i p}^*(1) h_1 \chi_{m_i q}(1) dv_1, \quad (3.15)$$

the two-electron integrals

$$\begin{aligned} \langle pq|rs \rangle &= \langle p(1)q(1)|r(2)s(2) \rangle \\ &= \int \chi_{m_i p}^*(1) \chi_{m_i r}^*(2) g_{12} \chi_{m_i q}(1) \chi_{m_i s}(2) dv_1 dv_2 \end{aligned} \quad (3.16)$$

and the supermatrices

$$P_{m_i p q, m_j r s} = \langle pq|rs \rangle - (1/4) (\langle ps|qr \rangle + \langle pr|qs \rangle), \quad (3.17)$$

TABLE I. The complex basis functions,  $\chi_{m_i}$ , for  $s$ ,  $p$ , and  $d$  orbitals.

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$$\begin{aligned} \chi_{0i} &= g_s = N_s \exp(-\alpha_i r^2) \\ \chi_{-1i} &= 1/2^{1/2} (g_x - i g_y) = N_p / 2^{1/2} (x - iy) \exp(-\alpha_i r^2) \\ \chi_{+1i} &= 1/2^{1/2} (g_x + i g_y) = N_p / 2^{1/2} (x + iy) \exp(-\alpha_i r^2) \\ \chi_{-2i} &= 1/5^{1/2} (g_{x^2-y^2} - 2i g_{xy}) \\ &= 1/5^{1/2} [N_x^2 - y^2 (x^2 - y^2) - 2i N_{xy} xy] \exp(-\alpha_i r^2) \\ \chi_{+2i} &= 1/5^{1/2} (g_{x^2-y^2} + 2i g_{xy}) \\ &= 1/5^{1/2} [N_x^2 - y^2 (x^2 - y^2) + 2i N_{xy} xy] \exp(-\alpha_i r^2) \end{aligned}$$


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The functions  $g$  are the corresponding normalized Cartesian Gaussian functions. The normalization coefficients,  $N$ , are defined in the Appendix.

we obtain the total energy

$$\begin{aligned}
 E &= 2 \sum_{n, m_l}^{occ} \sum_{p, q \in m_l} C_{nm_l p} C_{nm_l q} H_{m_l p q} \\
 &+ 2 \sum_{n, m_l}^{occ} \sum_{n', m'_l}^{occ} \sum_{p, q \in m_l} \sum_{r, s \in m'_l} \\
 &\cdot C_{nm_l p} C_{nm_l q} C_{n' m'_l r} C_{n' m'_l s} \\
 &\cdot [\langle pq|rs\rangle - (1/4)(\langle ps|qr\rangle + \langle pr|qs\rangle)] \\
 &= \sum_{m_l}^{occ} \sum_{p, q} D_{m_l p q} H_{m_l p q} + (1/2) \sum_{m_l}^{occ} \sum_{m'_l}^{occ} \sum_{p, q} \sum_{r, s} D_{m_l p q} D_{m'_l r s} P_{m_l p q, m'_l r s}. \quad (3.18)
 \end{aligned}$$

This closed-shell expression is applicable if all states with the same  $m_l$  (not  $|m_l|$ ) are filled. The calculation of the integrals is described in the Appendix.

### 3.2. Angular Momentum Coupling and Open Shells

The orbital angular momentum of the 2D atom is obtained by algebraic addition

$$M_L = \sum_i^{occ} m_l; \quad (3.19)$$

similarly, the total spin

$$M_S = \sum_i^{occ} m_s, \quad (3.20)$$

when

$$M = M_L + M_S. \quad (3.21)$$

It should be noted that the existence of two space orbitals (e.g.,  $\phi_{n-1}$  and  $\phi_{n+1}$  for  $np^2$ ), with two spin components,  $m_s$ , for each ( $\alpha$  and  $\beta$ ), inevitably leads to four states. Of them, three (with  $M_S = -1, 0, +1$ ) have the same and one has (with  $M_S = 0$ ) a different energy. Thus, the assumptions made still would allow a vector total spin

$$\mathbf{S} = \sum_i^{occ} \mathbf{s}_i, \quad (3.22)$$

with

$$\mathbf{S}^2 = S(S + 1).$$

In other words, we treat here, as an ad hoc assumption, spin and statistics in exactly the same way as in 3D. This permits us to study atomic physics and chemical periodicity with one, and only one, drastic change in the assumptions, namely, 2D vs. 3D.

With  $L = |M_L|$ , we can still use the term symbol

$$^{2S+1}L.$$

The terms for the present electron configurations are given in Tables II and III. The corresponding wave functions, in terms of one or two Slater determinants, are given in Table IV.

The core-core, core-valence, and valence-valence contributions to the total energy become for  $N$  occupied closed shells and  $M$  occupied open shells

$$\begin{aligned}
 E = & 2 \sum_k^N I_k + \sum_{k,l=1}^N (2J_{kl} - K_{kl}) \\
 & + \sum_m^M I_m + \sum_{m,n=1}^M [(1/2)a_{\sigma\mu} J_{mn} - (1/4)b_{\sigma\mu} K_{mn}] \\
 & + 2 \sum_{k=1}^N \sum_{m=1}^M (2J_{km} - K_{km}). \quad (3.23)
 \end{aligned}$$

Here  $\sigma$  and  $\mu$  label the two open-shell states  $n, m_l$  and  $n', m'_l$ , respectively.

The coupling constants  $1 - a$  and  $1 - b$  (Table V) are given to the program as fractions,  $n_1/n_2$ . The treatment parallels the 3D one in Clementi [19], Roothaan

TABLE II. Multiplets for equivalent  $s$ ,  $p$ , and  $d$  electrons.

Configuration	Terms
$s^1$	$^2S$
$s^2$	$^1S$
$p^1, p^3$	$^2P$
$p^2$	$^1D, ^3S, ^1S$
$p^4$	$^1S$
$d^1, d^3$	$^2D$
$d^2$	$^1G, ^3S, ^1S$
$d^4$	$^1S$

TABLE III. Multiplets for nonequivalent electrons.

Configuration	Terms	Configuration	Terms
$ss'$	$^3S, ^1S$	$pd, p^3d, pd^3, p^3d^3$	$^3F, ^1F, ^3P, ^1P$
$sp, sp^3$	$^3P, ^1P$	$p^2d, p^2d^3$	$^2G, ^4D, ^2D, ^2S$
$sp^2$	$^2D, ^4S, ^2S$	$pd^2, p^3d^2$	$^2H, ^2F, ^4P, ^2P$
$sd, sd^3$	$^3D, ^1D$	$p^2d^2$	$^1I, ^3G, ^1G, ^3D, ^1D, ^3S, ^3S, ^1S$
$sd^2$	$^2G, ^4S, ^2S$	$dd', d^3d', d^3d'^3$	$^3G, ^1G, ^3S, ^1S$
$pp', p^3p', p^3p'^3$	$^3D, ^1D, ^3S, ^1D$	$d^2d', d^2d'^3$	$^2I, ^4D, ^2D$
$p^2p', p^2p'^3$	$^2F, ^4P, ^2P$	$d^2d'^2$	$^1L, ^3G, ^1G, ^5S, ^3S, ^1S$
$p^2p'^2$	$^1G, ^3D, ^1D, ^3S, ^3S, ^1S$		

TABLE IV. The simplest wave functions for open-shell states.

Conf.	Term	$M$	
$np^2$	$^1D$	-2	$ \phi_{n-1}\bar{\phi}_{n-1} $
		2	$ \phi_{n+1}\bar{\phi}_{n+1} $
	$^3S$	0	$ \phi_{n-1}\bar{\phi}_{n+1}  -  \bar{\phi}_{n-1}\phi_{n+1} $
		-1	$ \bar{\phi}_{n-1}\bar{\phi}_{n+1} $
		0	$ \phi_{n-1}\bar{\phi}_{n+1}  +  \bar{\phi}_{n-1}\phi_{n+1} $
	1	$ \phi_{n-1}\phi_{n+1} $	

The bar indicates  $\beta$  spin.

TABLE V. Coupling constants  $a$  and  $b$  [Eq. (3.27)] for the configurations with one, two, or three open subshells ( $\sigma, \mu = 0, \pm 1, \pm 2$ ).

Configuration	State	$a_{\sigma\sigma}$	$a_{\sigma\mu}$	$b_{\sigma\sigma}$	$b_{\sigma\mu}$
$s, p, d, p^3, d^3$	$^2L$	0	-	0	-
$p^2, d^2, sd^3$	$^1L$	0	1	0	-2
	$^3L$	1	1	2	2
$sd^2(^3S)$	$^4S$	1	1	2	2
	$^2S$	1	1	2	$0^a$
					$2^b$

<sup>a</sup> $b_{0-2}$  and  $b_{0+2}$ .

<sup>b</sup> $b_{-2+2}$ .

and Bagus [20], or Veillard [21]. The final energy expression, used by the program, is

$$\begin{aligned}
 E = & \sum_{\sigma} \sum_{\rho q} D_{\sigma\rho q}^T H_{\sigma\rho q} \\
 & + (1/2) \sum_{\sigma\mu} \sum_{\rho qrs} D_{\sigma\rho q}^T P_{\sigma\rho q, \mu rs} D_{\mu rs}^T \\
 & - (1/2) \sum_{\sigma\mu} \sum_{\rho qrs} D_{\sigma\rho q}^o Q_{\sigma\rho q, \mu rs} D_{\mu rs}^o. \tag{3.24}
 \end{aligned}$$

Here, the closed-shell density matrix,  $D_{\sigma\rho q}^c$ , is given by (3.14), the open-shell density matrix

$$D_{\sigma\rho q}^o = \sum_{m=1}^M C_{\sigma mp} C_{\sigma mq}, \tag{3.25}$$

the total density matrix

$$D_{\sigma\rho q}^T = D_{\sigma\rho q}^c + D_{\sigma\rho q}^o, \tag{3.26}$$

and the supermatrices

$$Q_{\sigma\rho q, \mu rs} = (1 - a_{\sigma\mu})\langle pq|rs\rangle - (1/4)(1 - b_{\sigma\mu})(\langle ps|qr\rangle + \langle pr|qs\rangle). \tag{3.27}$$

The supermatrices  $P$  and the integrals  $H$  are defined above.

### 3.3. The Implementation

The program is a modified version of Pitzer's [22] 3D program. To saturate the basis, even-tempered Gaussian functions with orbital exponents

$$\alpha_i = \alpha_0 \beta^n \quad (3.28)$$

were used. With  $\beta = 2$ , the total energies and virial ratios in Tables VI and VII were obtained.

## 4. Results and Discussion

### 4.1. The Filling Order

For the  $s$  elements, we use the same chemical symbols as in the 3D case (H, He, Li, Be, . . .). Similarly, the  $s^2p^1$  elements are called B, Al, and Ga. The  $s^2p^2$

TABLE VI. Calculated HF total energies for  $Z = 1-14$ ;  $\beta = 2$ .

Atom	State	$-E_T/\text{a.u.}$	$-V/T$	$N_s$	$N_p$	$\alpha_{0s}$	$\alpha_{0p}$
$_1\text{H}$	$^2S$	1.99999993	2.00000012	32	—	0.006	—
$_1\text{H}^-$	$^1S$	2.06144747 2.0616 <sup>a</sup>	2.00000004	32	—	0.003	—
$_2\text{He}$	$^1S$	11.70208627 11.63665 <sup>b</sup> 11.70208779 <sup>a</sup>	2.00000027	32	—	0.003	—
$_3\text{Li}$	$^2S$	29.66839589	2.00000023	36	—	0.0005	—
$_4\text{Be}$	$^1S$	56.50163197	2.00000004	36	—	0.0005	—
$_5\text{B}$	$^2P$	92.75230862	2.00000061	36	26	0.0005	0.0005
$_6\text{N}$	$^1S$	138.66560554	2.00000087	36	26	0.0005	0.0005
	$^1D$	138.85968197	2.00000086	36	26	0.0005	0.0005
	$^3S$	139.07735545	2.00000086	36	26	0.0005	0.0005
$_7\text{F}$	$^2P$	195.57572920	2.00000116	36	26	0.0005	0.0005
$_8\text{Ne}$	$^1S$	263.22579119	2.00000147	36	26	0.0005	0.0005
$_9\text{Na}$	$^2S$	341.94421060 341.94444444	2.00000179 2.00000046	36 40	26 26	0.0005 0.000125	0.0005 0.0005
$_{10}\text{Mg}$	$^1S$	431.75647769	2.00000222	36	26	0.0005	0.0005
$_{11}\text{Al}$	$^2P$	532.89611460	2.00000265	36	26	0.0005	0.0005
$_{12}\text{P}$	$^1S$	645.37828334	2.00000312	36	26	0.0005	0.0005
	$^1D$	645.47988535	2.00000312	36	26	0.0005	0.0005
	$^3S$	645.59574004	2.00000312	36	26	0.0005	0.0005
$_{13}\text{Cl}$	$^2P$	769.81487332	2.00000361	36	26	0.0005	0.0005
$_{14}\text{Ar}$	$^1S$	905.98360472	2.00000416	36	26	0.0005	0.0005

<sup>a</sup>Ref. 9.

<sup>b</sup>Single-Zeta STO result from Ref. 7.

TABLE VII. Calculated HF total energies for  $Z = 15-24$ ;  $\beta = 2$ .

Atom	Configuration	State	$-E_T/\text{a.u.}$	$-V/T$	$N_s$ $\alpha_{0s}$	$N_p$ $\alpha_{0p}$	$N_d$ $\alpha_{0d}$
15K	$4s^1$	$^2S$	1054.059501	2.000001	40	26	—
					0.000125	0.0005	—
16Ca	$3d^1$	$^2D$	1054.017426	2.000001	40	26	20
					0.000125	0.0005	0.0000625
16Ca	$4s^2$	$^1S$	1214.035817	2.000001	40	26	—
					0.000125	0.0005	—
17Sc	$4s^1 3d^1$	$^3D$	1214.030962	2.000001	40	26	20
					0.000125	0.0005	0.001
17Sc	$4s^2 3d^1$	$^2D$	1385.062704	2.001536	27	21	18
					0.001	0.0005	0.001
17Sc	$4s^2 4p^1$	$^2P$	1385.005692	2.001537	27	21	—
					0.001	0.0005	—
18Mn	$4s^1 3d^2$	$^2S$	1385.015176	2.001536	27	21	18
					0.001	0.0005	0.001
18Mn	$4s^2 3d^2$	$^1S$	1569.110171	2.001716	27	16	18
					0.001	0.0005	0.001
18Mn	$4s^2 3d^2$	$^1D$	1569.189583	2.001716	27	16	18
					0.001	0.016	0.001
18Mn	$4s^2 3d^2$	$^3S$	1569.276261	2.001716	27	16	18
					0.001	0.016	0.001
18Mn	$4s^1 3d^3$	$^1D$	1569.121615	2.001716	27	16	18
					0.001	0.016	0.001
18Mn	$4s^1 3d^3$	$^3D$	1569.150883	2.001716	27	16	18
					0.001	0.016	0.001
19Cu	$4s^2 3d^3$	$^2D$	1765.848244	2.001907	27	16	18
					0.001	0.016	0.001
19Cu	$4s^1 3d^4$	$^2S$	1765.735087	2.001907	27	16	18
					0.001	0.016	0.001
20Zn	$4s^2 3d^4$	$^1S$	1975.117683	2.002109	27	16	18
					0.001	0.016	0.001
21Ga	$3d^4 4p^1$	$^2P$	2197.252163	2.002321	27	20	18
					0.001	0.001	0.001
22As	$3d^4 4p^2$	$^1D$	2432.126757	2.002546	27	20	18
					0.001	0.001	0.001
22As	$3d^4 4p^2$	$^3S$	2432.207803	2.002546	27	20	18
					0.001	0.001	0.001
23Br	$3d^4 4p^3$	$^2P$	2679.888349	2.002782	27	20	18
					0.001	0.001	0.001
23Br	$3d^3 4p^4$	$^2D$	2678.896328	2.002785	27	20	18
					0.001	0.001	0.001
24Kr	$3d^4 4p^4$	$^1S$	2940.536635	2.003031	27	20	18
					0.001	0.001	0.001
24Kr	$3d^4 4p^4$	$^1S$	2944.793598	2.000045	34	26	22
					0.0005	0.001	0.001

ones could carry the 3D group 14 names (C, Si, Ge) or, being the half-filled  $p$ -shell, the group 15 ones (N, P, As). We choose the latter alternative. The present  $s^2p^3$  atoms, with one  $p$  hole, are the 2D halogens, F, Cl, and Br. The  $s^2p^4$  rare gases are called Ne, Ar, and Kr. Analogously, the first transition elements are called Sc, Mn, Ni, and Cu.

The first open question is whether  ${}_{15}\text{K}$  has a  $4s^1$  or  $3d^1$  ground state. From Table VII, we see that the  $4s^1 E_T$  lies 0.042075 a.u. below  $3d^1$ . Similarly, the difference of the  $4s$  and  $3d$  eigenvalues of  $-0.105859$  and  $-0.063745$  a.u. becomes 0.042114 a.u. Therefore,  $4s$  is occupied before  $3d$ , in 2D.

For the next element,  ${}_{16}\text{Ca}$ , the  $4s^1 3d^1 {}^3D$  state lies only 0.004855 a.u. above the  $4s^2 {}^1S$  ground state. The  $4s$  and  $3d \langle r \rangle$  are 5.01512 and 5.36659 and the  $-\epsilon$  0.167881 and 0.099245 a.u., respectively. Thus, the Ca  $3d$  still has not collapsed to the inner potential well.

Next, for  ${}_{17}\text{Sc}$ , the  $3d^1 E_T$  lies 0.057012 a.u. below the  $4p^1$  one. The difference of the  $d$  and  $p$  eigenvalues 0.293781 and 0.149648 a.u., respectively, is now 0.144133 a.u., in this three-valence-electron case. Thus, at the HF level, the  $3d$  shell is occupied before  $4p$ .

As  $d^2$  is the half-filled shell, we also considered for  ${}_{17}\text{Sc}$  the state  $4s^1(3d_{-2})^1(3d_2)^1 {}^4S$ . It has a higher spin and lies at the HF level slightly (0.016 a.u.) below the  $4s^2 3d^1$  configuration, in complete analogy with the 3D  ${}_{24}\text{Cr}$   $4s^1 3d^5$  ground state, but in contrast to the 3D  ${}_{21}\text{Sc}$   $4s^2 3d^1$  one.

The 2D  ${}_{18}\text{Mn}$  has a  $4s^2 3d^2 {}^3S$  ground state, analogous to the 3D  ${}_{25}\text{Mn}$   $4s^2 3d^5 {}^6S$  one, both  $d$ -shells being half-filled. The  $4s^1 3d^3$  lie higher.

For  ${}_{19}\text{Cu}$ , the question is whether the hole is put in the  $4s$  or  $3d$  shell. In 2D, the  $d$  hole is preferred, rather like for the 3D  ${}_{28}\text{Ni}$ ,  $4s^2 3d^8$ , but in contrast to the 3D  ${}_{29}\text{Cu}$ ,  $4s^1 3d^{10}$ . Thus, there is no clear-cut, monovalent  $4s^1$  coinage metal, like copper, in 2D. For  ${}_{20}\text{Zn}$ , there is no choice but  $4s^2 3d^4$ .

The  ${}_{21}\text{Ga}$   $4p^1$  configuration is obvious. So is the  ${}_{22}\text{As}$   $4p^2$  one, whose  ${}^3S$  ground state conforms to Hund's rule. The  ${}_{23}\text{Br}$   $4p^3$  halogen and the  ${}_{24}\text{Kr}$   $4p^4$  rare gas complete this period.

## 4.2. Partial-screening Effects

The best-known partial-screening effect in the usual 3D periodic system is the "lanthanide contraction," i.e., the effect on a valence electron between  $6s^2$  Ba and  $4f^{14}6s^2$  Yb, for instance. The corresponding  $d$ -electron or transition-metal contraction is also well known [23]. In the present case, the simplest example on this phenomenon is the difference between the  $1s^2 2s^2 3s^1 Z = 5$  "pseudo-Na" and actual  $1s^2 2s^2 2p^4 3s^1$   ${}^9\text{Na}$ . Their  $3s$  orbital energies are  $-0.138$  and  $-0.176$  a.u. and average radii 5.525 and 4.279 a.u., respectively. This is an example of partial screening of the  $3s$  valence electron by the  $2p$  shell.

As another example, we considered the  $1s^2 2s^2 2p^4 3s^2 3p^4 4s^2 4p^1 Z = 17$  "pseudo-Ga," occurring in Table VII as the  ${}^2P$  state of  ${}_{17}\text{Sc}$ . The  $\langle r \rangle_{4p}$  are 4.829 and 4.372 a.u., and the  $-\epsilon$ , 0.1496 and 0.1583 a.u. for "pseudo-Ga" and  ${}_{21}\text{Ga}$ , respectively. This is an example of partial screening of the  $4p$  valence electron by the  $3d$  shell, i.e., a "transition-metal contraction" (cf. [23]).

### 4.3. Orbital Energies

The 2D and 3D energies of the highest occupied orbital are compared in Figure 4. It is seen that the  $1s$ ,  $2s$ , and two first  $2p$  elements are more strongly bound in 2D for H and He by a factor of four. The later elements F—Kr (except Al) are more strongly bound in 3D.

Note that we jump here, for 3D, from  $p^1$  to  $p^3$  to  $p^5$  to  $p^6$  and similarly from  $d^1$  to  $d^5$  to  $d^9$  to  $d^{10}$ , compared to the 2D  $p^1$ – $p^4$  and  $d^1$ – $d^4$ .

### 4.4. Valence Orbital Radii

The 2D valence orbital radii are shown in Figure 5. The very small size of the  $1s$  shell is again conspicuous. The gradual increase of the  $ns$  and  $np$  radii for  $n = 2$ – $4$  resembles that in 3D. The  ${}_{17}\text{Sc}$   $4s$  and  $3d$  radii are out-of-line due to the  $s^1d^2$  configuration, different from the  $s^2d^k$  ones of the later transition metals. For the  $s^2d^1$  state,  $\langle r \rangle = 1.8739$  a.u. and  $-\epsilon = 0.1149$  a.u.; these values give a systematic trend with the  $Z = 18$ – $20$   $s^2d^n$  results.

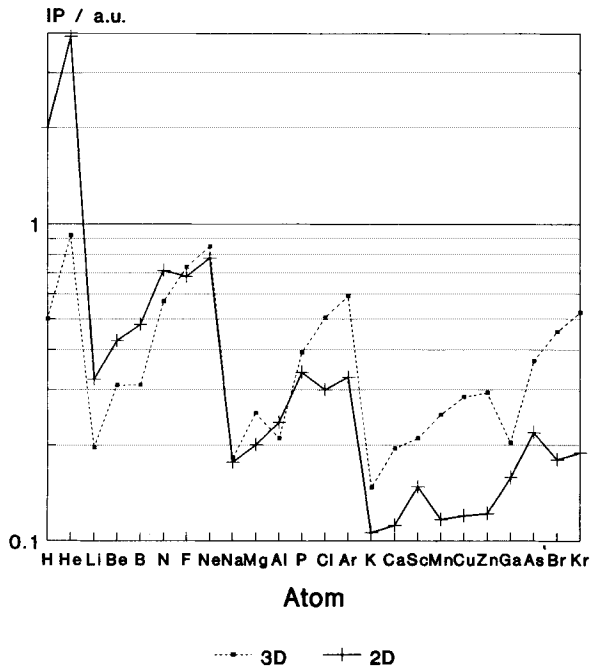


Figure 4. The highest occupied orbital energy in the HF model for the first 2D elements and their 3D analogs (from Froese Fischer [24]). In cases like 2D F  $[(2p_{-1})^2(2p_{+1})^1]$ , a weighed average is taken.

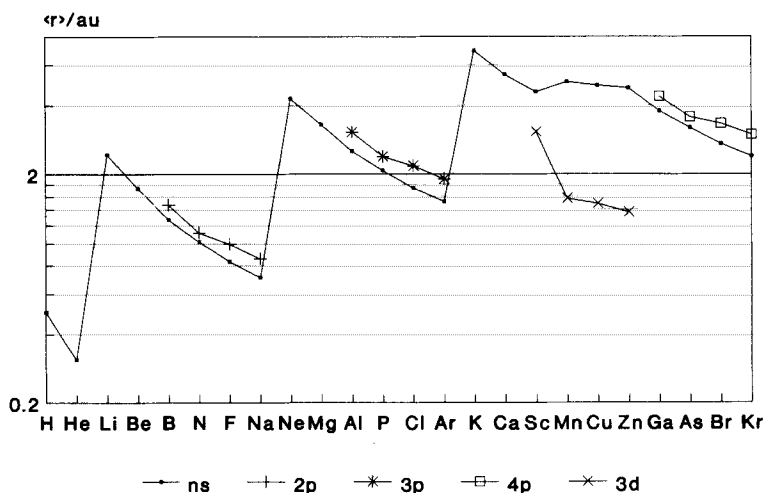


Figure 5. The average radii,  $\langle r \rangle$ , of the  $ns$ ,  $np$ , and  $(n - 1)d$  valence shells.

The ratio of the  $4s$  and  $3d$  radii for the  $s^2$  configuration of Cu is  $4.883/1.488 = 3.282$  and  $2.973/0.918 = 3.238$  in 2D and 3D [24], respectively. The two ratios are very similar.

In Figure 5, the  $2p$  radii are clearly larger than the  $2s$  ones. It is interesting to compare their ratio in 2D and 3D (see Table VIII). In 3D, the ratio  $R = \langle r \rangle_{2p} / \langle r \rangle_{2s}$  is rather close to 1, and the ratio  $r_{max}(2p) / r_{max}(2s)$  is below 1 for the elements C—Ne and above [25]. This similarity of the  $2s$  and  $2p$  radii and of their energies explains the facile multiple bonding of the 2nd-row elements (see [23]). An intuitive explanation is the lack of “primogenic repulsion” by inner  $p$ -shell on the  $2p$ .

In 2D, the ratio  $R$  is somewhat larger than in 3D and the increase from  $n = 2$  to  $n = 3$  is less conspicuous. The 2D B and N could still form good multiple bonds, as surmised by Laitinen and Pakkanen [1].

## 5. Conclusions

The central conclusion is that in these 2D model systems (for which P.W. Atkins proposed the name “flatoms”) the first,  $3d$  shell indeed is occupied after the  $3s$ ,  $3p$ , and  $4s$  ones, as in the 3D case. The reason that this happens, and that  $4s$  is not above  $3d$ , or, to the contrary, even  $4p$  below  $3d$ , is the hydrogenlike degeneracy of the  $n = 3$  levels and comparable screening effects for 2D and 3D.

Minor differences between 2D and 3D are found in the filling order for  $3d$  transition elements where  $4s^1 3d^2$  and  $4s^2 3d^3$  configurations are preferred for “Sc” and “Cu,” respectively.

The biggest difference is the very small radius and large binding energy of the 2D  $1s$  shell, making the 2D hydrogen a “superhalogen” or, alternatively, a “di-

TABLE VIII. Valence orbital average radii in 2D and in 3D [24] and the ratio  $R = \langle r \rangle_{np} / \langle r \rangle_{ns}$ .

Case	Atom	$\langle r \rangle_{ns}$	$\langle r \rangle_{np}$	$R$
2D	B( $2p^1$ )	1.26927	1.46603	1.15502
	N( $2p^2$ )	1.01589	1.11062	1.09325
	F( $2p^3$ )	0.83137	0.99317	1.19462
	Ne( $2p^4$ )	0.70873	0.85589	1.20764
	Al( $3p^1$ )	2.51582	3.04754	1.21135
3D	B( $2p^1$ )	1.97706	2.20476	1.11517
	C( $2p^2$ )	1.58934	1.71449	1.07874
	N( $2p^3$ )	1.33228	1.40963	1.05806
	O( $2p^4$ )	1.14196	1.23220	1.07902
	F( $2p^5$ )	1.00109	1.08479	1.08361
	Ne( $2p^6$ )	0.89211	0.96527	1.08201
	Al( $3p^1$ )	2.59928	3.43389	1.32109

atomic inert gas”, an unknown concept in 3D. The corresponding diatomic molecule would have a (minimal basis Heitler–London,  $\zeta = 1$ ) bond length of only 0.37 a.u. and the enormous dissociation energy of 1.25 a.u. [8]. Thus, one could speculate that the 2D water could be spontaneously reduced to  $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ . The 2D He analogously is a “superinert gas.” The 2D  $2s$  and early  $2p$  elements still have higher binding energies than do the 3D ones. For later elements, the 3D binding energies are larger.

Given the tendency of the  $1s$  atoms to become small and strongly bound when  $D$  decreases, the small size of the actual H and He could be seen as a tail of this trend for  $D = 3$ .

### Appendix

The expressions for the required integrals over the Gaussian Cartesian functions

$$\chi_{m_l p} = N_p x^{l_p} y^{m_p} \exp(-\alpha_p r^2), \quad (\text{A.1})$$

$$N_p = \{(2\alpha_p)^{(l_p+m_p+1)} / [\Gamma((2l_p+1)/2)\Gamma((2m_p+1)/2)]\}^{1/2} \quad (\text{A.2})$$

become

1. The overlap integral:

$$\langle p | q \rangle = N_p N_q S(l_p, m_p; l_q, m_q), \quad (\text{A.3})$$

$$S(l_p, m_p; l_q, m_q) = (\alpha_p + \alpha_q)^{-(l_p+l_q+m_p+m_q+2)/2} \cdot \Gamma((l_p+l_q+1)/2)\Gamma((m_p+m_q+1)/2), \quad (\text{A.4})$$

for  $l_p + l_q$  and  $m_p + m_q$  even, and zero otherwise.

The gamma function:

$$\begin{aligned}\Gamma(n + 1/2) &= (2n - 1)!! \pi^{1/2}/2^n, \\ (-1)!! &= 1.\end{aligned}\tag{A.5}$$

2. The kinetic energy integral:

$$\begin{aligned}\langle p | - (1/2)\nabla^2 | q \rangle &= -(1/2) \{ l_q(l_q - 1)S(l_p, m_p; l_q - 2, m_q) \\ &\quad - 4\alpha_q(l_q + m_q + 1)S(l_p, m_p; l_q, m_q) \\ &\quad + 4\alpha_q^2[S(l_p, m_p; l_q + 2, m_q) + S(l_p, m_p; l_q, m_q + 2)] \\ &\quad + m_q(m_q - 1)S(l_p, m_p; l_q, m_q - 2) \}.\end{aligned}\tag{A.6}$$

Here, the  $S$  functions are the nonnormalized overlap integrals, defined in Eq. (A.4).

3. The nuclear attraction integral:

$$\begin{aligned}\langle p | r^{-1} | q \rangle &= N_p N_q \Gamma((l_p + l_q + 1)/2) \Gamma((m_p + m_q + 1)/2) \\ &\quad \cdot \Gamma((l_p + l_q + m_p + m_q + 1)/2) (\alpha_p + \alpha_q)^{-(l_p + l_q + m_p + m_q + 1)/2} \\ &\quad \div ((l_p + l_q + m_p + m_q)/2)!,\end{aligned}\tag{A.7}$$

for  $l_p + l_q$  and  $m_p + m_q$  even, and zero otherwise.

4. The electron–electron integral. Here, three cases arise:

(a)  $\delta = 0$ ,

$$\begin{aligned}\langle pqrs \rangle &= \langle p(1)q(1) | r_{12}^{-1} | r(2)s(2) \rangle \\ &= \pi^{1/2} (l_r + l_s)! (m_r + m_s)! \\ &\quad \cdot \sum_{k=0}^{k_{up}} \Gamma((L - 2k + 1)/2) / [k! (l_r + l_s - 2k)! 2^{2k}] \\ &\quad \cdot \sum_{l=0}^{l_{up}} \Gamma((M - 2l + 1)/2) / [l! (m_r + m_s - 2l)! 2^{2l}] \\ &\quad \cdot B(\mu, \sigma - \mu) [(\alpha_p + \alpha_q) (\alpha_r + \alpha_s)]^{-\mu - \sigma} A^{-\mu}.\end{aligned}\tag{A.8}$$

(b)  $\delta < 0$ ,

$$\begin{aligned}\langle pqrs \rangle &= \pi^{1/2} (l_r + l_s)! (m_r + m_s)! \\ &\quad \cdot \sum_{k=0}^{k_{up}} \Gamma((L - 2k + 1)/2) / [k! (l_r + l_s - 2k)! 2^{2k}] \\ &\quad \cdot \sum_{l=0}^{l_{up}} \Gamma((M - 2l + 1)/2) / [l! (m_r + m_s - 2l)! 2^{2l}] \\ &\quad \cdot B(\mu, \delta - \mu + \sigma) {}_2F_1(\delta, \mu; \delta + \sigma; x) \\ &\quad \cdot (\alpha_p + \alpha_q)^{\mu - \sigma} (\alpha_r + \alpha_s)^{\mu - \delta - \sigma} A^{-\mu}.\end{aligned}\tag{A.9}$$

(c)  $\delta > 0$ ,

$$\begin{aligned}
\langle pqrs \rangle &= \pi^{1/2} (l_p + l_q)! (m_p + m_q)! \\
&\cdot \sum_{k=0}^{k_{up}} \Gamma((L - 2k + 1)/2) / [k! (l_p + l_q - 2k)! 2^{2k}] \\
&\cdot \sum_{l=0}^{l_{up}} \Gamma((M - 2l + 1)/2) / [l! (m_p + m_q - 2l)! 2^{2l}] \\
&\cdot B(\mu', -\delta - \mu' + \sigma) {}_2F_1(-\delta, \mu'; \sigma - \delta; x') \\
&\cdot (\alpha_p + \alpha_q)^{\mu' - \sigma + \delta} (\alpha_r + \alpha_s)^{\mu' - \sigma} A^{-\mu'}.
\end{aligned} \tag{A.10}$$

With

$$\begin{aligned}
k_{up} &= [(l_r + l_s)/2], & l_{up} &= [(m_r + m_s)/2], \\
k_{up'} &= [(l_p + l_q)/2], & l_{up'} &= [(m_p + m_q)/2], \\
L &= l_p + l_q + l_r + l_s, & M &= m_p + m_q + m_r + m_s, \\
\delta &= [-(l_p + l_q) + l_r + l_s - (m_p + m_q) + m_r + m_s]/2, \\
\mu &= l_r + l_s + m_r + m_s - 2k - 2l + 1/2, & \mu' &= l_p + l_q \\
&\quad + m_p + m_q - 2k - 2l + 1/2, \\
\sigma &= (L + M - 2k - 2l + 2)/2, \\
A &= \alpha_p + \alpha_q + \alpha_r + \alpha_s, \\
x &= (\alpha_r + \alpha_s)/A, & x' &= (\alpha_p + \alpha_q)/A, \\
B(m, n) &= (m - 1)! (n - 1)! / (m + n - 1)!, \\
{}_2F_1(a, b; c; x) &= 1 + a \cdot b / (1 \cdot c) \cdot x \\
&\quad + a \cdot (a + 1) \cdot b \cdot (b + 1) / (1 \cdot 2 \cdot c \cdot (c + 1)) \cdot x^2 + \dots
\end{aligned} \tag{A.11}$$

(A.12)

**Note added in proof:**

Two further papers on relativistic [26–27] and one on non-relativistic [28] 2D hydrogen atoms have recently appeared.

### Bibliography

- [1] R. Laitinen and T. A. Pakkanen, in *XX International Chemistry Olympiad Finland 1988*, Report, (1988) p. 52.
- [2] P. Pyykkö, in *The Effects of Relativity in Atoms, Molecules and the Solid-State*, S. Wilson, I. P. Grant, and B. L. Gyorffy, Eds. (Plenum, New York and London, 1991).
- [3] W. Kohn and J. M. Luttinger, *Phys. Rev.* **98**, 915 (1955).
- [4] M. Shinada and S. Sugano, *J. Phys. Soc. Jpn.* **21**, 1936 (1966).
- [5] A. H. MacDonald and D. S. Ritchie, *Phys. Rev. B* **33**, 8336 (1986).
- [6] D. D. Frantz and D. R. Herschbach, *J. Chem. Phys.* **92**, 6668 (1990).
- [7] E. A. de Andrada e Silva, I. C. da Cunha Lima, and A. Ferreira da Silva, *Int. J. Quantum Chem.* **30**, 685 (1986).

- [8] M. Fabbri and A. Ferreira da Silva, *Phys. Rev. A* **32**, 1870 (1985).
- [9] J. G. Loeser and D. R. Herschbach, *J. Chem. Phys.* **84**, 3893 (1986).
- [10] J. G. Loeser, *J. Chem. Phys.* **86**, 5635 (1987).
- [11] J. M. Jauch and E. L. Hill, *Phys. Rev.* **57**, 641 (1940).
- [12] R. E. Moss, *Am. J. Phys.* **55**, 397 (1987).
- [13] C. A. Coulson and A. Joseph, *Rev. Mod. Phys.* **39**, 838 (1967).
- [14] J. Cížek and J. Paldus, *Int. J. Quantum Chem.* **12**, 875 (1977).
- [15] S. A. Bruce, *Am. J. Phys.* **54**, 446 (1968).
- [16] K. Sokalski, *Acta Phys. Polon.* **A76**, 901 (1989).
- [17] A. S. Davydov, *Quantum Mechanics*, 2nd ed. (Pergamon, Oxford, 1976), Chapt. 58.
- [18] G. F. Kventzel and J. Katriel, *Phys. Rev. A* **24**, 2299 (1981).
- [19] E. Clementi, *Modern Techniques in Computational Chemistry* (ESCOM, Leiden, 1989).
- [20] C. C. J. Roothaan and P. S. Bagus, *Methods Comp. Phys.* **2**, 47 (1963).
- [21] A. Veillard, in *Computational Techniques in Quantum Chemistry and Physics*, G. H. F. Dierksen, B. T. Sutcliffe, and A. Veillard, Eds. (Reidel, Dordrecht, 1975), p. 239.
- [22] R. M. Pitzer, Quantum Chemistry Program Exchange, Indiana University, Program No. 587 (1990).
- [23] P. Pyykkö, *J. Chem. Res. (S)*, 380 (1979).
- [24] C. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).
- [25] J. P. Desclaux, *At. Data Nucl. Data Tables* **12**, 311 (1973).
- [26] M. K. F. Wong, *J. Math. Phys.* **31**, 1677 (1990).
- [27] S. H. Guo, X. L. Yang, F. T. Chan, K. W. Wong and W. Y. Ching, *Phys. Rev.* **A43**, 1197 (1991).
- [28] X. L. Yang, S. H. Guo, F. T. Chan, K. W. Wong and W. Y. Ching, *Phys. Rev.* **A43**, 1186 (1991).

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