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## EXPLICIT LARGE NUCLEAR CHARGE LIMIT OF ELECTRONIC GROUND STATES FOR Li, Be, B, C, N, O, F, Ne AND BASIC ASPECTS OF THE PERIODIC TABLE\*

GERO FRIESECKE<sup>†</sup> AND BENJAMIN D. GODDARD<sup>‡</sup>

**Abstract.** This paper is concerned with the Schrödinger equation for atoms and ions with  $N = 1$  to 10 electrons. In the asymptotic limit of large nuclear charge  $Z$ , we determine explicitly the low-lying energy levels and eigenstates. The asymptotic energies and wavefunctions are in good quantitative agreement with experimental data for positive ions, and in excellent qualitative agreement even for neutral atoms ( $Z = N$ ). In particular, the predicted ground state spin and angular momentum quantum numbers ( $^1S$  for He, Be, Ne,  $^2S$  for H and Li,  $^4S$  for N,  $^2P$  for B and F, and  $^3P$  for C and O) agree with experiment in every case. The asymptotic Schrödinger ground states agree, up to small corrections, with the semiempirical hydrogen orbital configurations developed by Bohr, Hund, and Slater to explain the periodic table. In rare cases where our results deviate from this picture, such as the ordering of the lowest  $^1D^o$  and  $^3S^o$  states of the carbon isoelectronic sequence, experiment confirms our predictions and not Hund's.

**Key words.** quantum chemistry, electronic structure, periodic table, Schrödinger equation, Hund's rules, Aufbau principle

**AMS subject classifications.** 81Q05, 81V45, 81R05

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**1. Introduction.** How do the striking chemical differences between some elements, and the similarities between others, emerge from the universal laws of quantum mechanics? In the physics and chemistry literature, this fundamental question is discussed on a semiempirical level, via the “hydrogen orbital configurations” developed by Bohr, Hund, and Slater (see, e.g., [Boh22, Hun25, Sla30, CS35, LL77, Sch01, AdP01]), or via numerical simulation of simplified quantum mechanical models (see, e.g., [Har28, Har57, FF77, TTST94, Joh05, BT86]). In this article, we address this question from a mathematical perspective.

The theoretical possibility of making chemically specific predictions was realized almost immediately after the Schrödinger equation had been introduced (see, e.g., [Har28, Dir29]). But we are not aware of previous rigorous results, as mathematical research on the basic quantum mechanical equations has hitherto focused overwhelmingly on universal, qualitative properties.

The perhaps most basic nonuniversal properties of atoms relevant to chemical behavior are the total spin and angular momentum quantum numbers  $S$  and  $L$  of the ground state, which describe the amount of symmetry under spin and spatial rotation. These two numbers not only determine the ground state dimension  $d$ , but, as argued below, they also allow one to predict, up to at most two possibilities, the group of the atom in the periodic table.

Other quantities of interest include the energy levels  $E_n$  and, more importantly, energy differences such as spectral gaps  $E_n - E_m$  (which govern the photon frequen-

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TABLE 1

Angular momentum and spin quantum numbers and dimension of the Schrödinger ground state for large  $Z$ , as calculated in this paper. All numbers agree with the experimental values for neutral atoms [RJK<sup>+</sup>07].

Isoelectronic sequence	H	He	Li	Be	B	C	N	O	F	Ne
Number of electrons	1	2	3	4	5	6	7	8	9	10
$L$	0	0	0	0	1	1	0	1	1	0
$S$	$\frac{1}{2}$	0	$\frac{1}{2}$	0	$\frac{1}{2}$	1	$\frac{3}{2}$	1	$\frac{1}{2}$	0
Chemist's notation	$2_S$	$1_S$	$2_S$	$1_S$	$2_P$	$3_P$	$4_S$	$3_P$	$2_P$	$1_S$
dim	2	1	2	1	6	9	4	9	6	1

cies which the atom can emit or absorb) and the ionization energy (whose striking empirical periodicities lay at the origin of the design of the periodic table).

Our principal result is that such quantities can be extracted analytically from the many-electron Schrödinger equation in a natural scaling limit. More precisely, we show that for ions with  $N = 1$  to 10 electrons, as the nuclear charge  $Z$  gets large, the low-lying energy levels and eigenstates converge to well-defined limits, which can be determined explicitly. In particular, this yields rigorous values of  $L$ ,  $S$ ,  $d$  for the ground state for all sufficiently large  $Z$ . See Theorems 3.1, 4.1, and 7.1 and Tables 1, 2, 15, and 16. We call the above fixed- $N$ , large- $Z$  limit the *isoelectronic limit*, because it is realized physically by an isoelectronic sequence such as Li, Be<sup>+</sup>, B<sup>++</sup>, etc. Note that this limit is different from the Thomas–Fermi limit  $N = Z \rightarrow \infty$ , which is of interest in other contexts but does not retain any chemical specificity.

The asymptotic levels and eigenstates are in good quantitative agreement with experimental data for positive ions, and in excellent qualitative agreement even for neutral atoms ( $Z = N$ ). In particular the predicted values of  $L$ ,  $S$ , and  $d$  (see Table 1) agree with the experimental atomic values [RJK<sup>+</sup>07] in all cases.

The asymptotic ground states we calculate (see Theorem 3.1) provide for the first time a mathematical justification of the celebrated semiempirical “hydrogen orbital configurations” developed notably by Bohr, Hund, and Slater to explain the periodic table. In our approach, none of the underlying nontrivial postulates (electrons filling hydrogen orbitals, shell and subshell formation, subshell ordering rules such as  $2s < 2p$ , Hund’s rules) need to be invoked, but are seen to emerge in a natural way. The only corrections are as follows (see sections 3.1 and 8 for a detailed discussion):

(1) Alongside each Slater determinant built from admissible hydrogen orbitals, the ground state must contain its orbit under the symmetry group  $SO(3) \times SU(2) \times \mathbb{Z}_2$  of the many-electron Schrödinger equation.

(2) For the three elements Be, B, C, a ten to twenty percent admixture of a particular “higher subshell” configuration is also present, an effect we term  $2s^2-2p^2$  resonance.

(3) In rare cases, such as that of the lowest  $1D^o$  and  $5S^o$  states of carbon, the ordering of excited states disagrees with the semiempirical Hund’s rules (with experiment confirming our orderings).

We now outline our mathematical strategy to obtain explicit asymptotic energy levels and eigenstates, focusing for simplicity on the ground state.

The first step is the derivation of a simplified model governing the asymptotics. This can be done via a scaling argument plus standard perturbation theory, as follows.

For fixed  $N$  and large  $Z$ , attraction of an electron by the nucleus dominates its interaction with the other electrons, so one expects the true ground state to be close to the ground state of the corresponding system with electron interaction turned off (which is known explicitly via hydrogen atom theory). After a little more thought, one realizes that this cannot be quite correct. The noninteracting ground state eigenspaces of atoms happen to be highly degenerate (see Table 3), but the underlying symmetry is broken by the interaction, so the true ground state eigenspaces should converge only to particular subspaces of them. (Experimentally, this phenomenon is well known from observed energy splittings.) Mathematically, we prove that the difference between the Schrödinger ground states and the ground states of the problem  $PHP\Psi = E\Psi$ , where  $P$  is the projector onto the noninteracting ground state but  $H$  is the full Hamiltonian (equation (2) below), tends to zero. We call this simplified problem the *PT model*, because it corresponds to (i) rescaling the problem so as to make the ground state of the reduced problem  $Z$ -independent, (ii) applying degenerate first order perturbation theory, (iii) undoing the rescaling. Physically it corresponds to resolving, within the noninteracting ground state eigenspace, the fully interacting problem.

The second step is to determine the lowest PT eigenspace. This requires a careful analysis of the interplay between hydrogen orbital formation (promoted by the Laplacian and electron-nuclei interaction), antisymmetry, spin, and electron interaction. More technically, the following difficulties arise:

(i) The noninteracting ground state, i.e., the state space of the PT model, is of somewhat daunting looking dimension, e.g., 70 in case of carbon (see Table 3).

(ii) The PT Hamiltonian  $PHP$  is easy to write down abstractly (as we have just done) but unknown; one needs to devise a method to determine it explicitly.

(iii) The PT model is a strongly interacting many-body model.

Difficulties (i) and (iii) are overcome via careful use of the symmetry group of the original equation and its representation theory in terms of many-body spin and angular momentum operators, which allows one to split the Hamiltonian  $PHP$  into small invariant blocks. (ii) is addressed by combining ideas from quantum chemistry which have not hitherto played a role in mathematical studies, such as Slater's rules [SO96] (which allow one to express the components of the Hamiltonian via six-dimensional integrals of a product of four hydrogen eigenstates and a Coulomb repulsion term), Fourier analysis (while the Fourier transform of individual hydrogen eigenstates is well known, here one requires the Fourier transform of pointwise products of these), and residue calculus. In principle, our methods apply to arbitrary atoms, except that the relevant  $PHP$  matrices can become significantly higher-dimensional.

One curious mathematical phenomenon we observe is that the Hamiltonian  $PHP$  arising in the  $Z \rightarrow \infty$  limit of quantum mechanics is always a rational matrix, despite  $H$  being a somewhat complicated partial differential operator and  $P$  a "transcendental" projector (onto tensor products of scaled hydrogen eigenfunctions such as  $\pi^{-1/2}e^{-|x|}$ ).

The structure of this paper is as follows. In section 2 we describe the basic quantum mechanical equations and their symmetry group. In section 3 we state the asymptotic limit of the Schrödinger ground states for Li to Ne (see Theorem 3.1). In sections 4 and 5, we justify the reduction to the PT model and determine explicitly its state space. Sections 6 and 7 contain more technical material: the explicit determination of the PT Hamiltonian and the derivation of Theorem 3.1, as well as of the excited states and levels of the PT model. Finally, sections 3.1 and 8 compare our results to experimental data and to methods in the physics and chemistry literature.

**2. Schrödinger equation and mathematical definition of basic quantities of chemical physics.** The exact (nonrelativistic, Born–Oppenheimer) time-independent Schrödinger equation for atoms and ions is

$$(1) \quad H\Psi = E\Psi,$$

where, for nuclear charge  $Z > 0$  and  $N$  electrons and in atomic units,

$$(2) \quad H = \sum_{i=1}^N \left( -\frac{1}{2} \Delta_{x_i} - \frac{Z}{|x_i|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|},$$

$E \in \mathbb{R}$ , and

$$(3) \quad \Psi \in L_a^2((\mathbb{R}^3 \times \mathbb{Z}_2)^N).$$

Here and below the  $x_i \in \mathbb{R}^3$  are electronic coordinates,  $s_i \in \mathbb{Z}_2 = \{\pm \frac{1}{2}\}$  are spin coordinates, and  $L_a^2$  is the usual Hilbert space of  $N$ -electron functions  $\Psi : (\mathbb{R}^3 \times \mathbb{Z}_2)^N \rightarrow \mathbb{C}$  which are square-integrable,

$$(4) \quad \int_{\mathbb{R}^{3N}} \sum_{(\mathbb{Z}_2)^N} |\Psi(x_1, s_1, \dots, x_N, s_N)|^2 = \|\Psi\|^2 < \infty,$$

and satisfy the antisymmetry principle that, for all  $i$  and  $j$ ,

$$(5) \quad \Psi(\dots, x_i, s_i, \dots, x_j, s_j, \dots) = -\Psi(\dots, x_j, s_j, \dots, x_i, s_i, \dots).$$

Mathematically,  $H$  is a bounded below, self-adjoint operator with domain  $L_a^2 \cap H^2$ , where  $H^2$  is the usual Sobolev space of  $L^2$  functions with second weak derivatives belonging to  $L^2$  [Kat51].

We are interested in the mathematical derivation of a number of quantities of basic physical and chemical interest, and begin by recalling how these are defined in terms of the Schrödinger equation (1).

**DEFINITION 1.** *An energy level of an atom or ion is an eigenvalue of the corresponding operator  $H$ . An eigenstate of the atom or ion is an eigenstate of  $H$  (i.e., a nonzero solution  $\Psi$  to (1) belonging to the domain of  $H$ ). By Zhislin's theorem ([Zhi60]; see [Fri03] for a short proof), for atoms ( $N = Z$ ) and positive ions ( $N < Z$ ) there exist countably many energy levels  $E_1 < E_2 < \dots$  below the bottom of the essential spectrum of  $H$ , the corresponding eigenspaces being finite-dimensional.  $E_1$  is called the ground state energy, and the corresponding eigenspace is known as the ground state. Eigenspaces corresponding to the higher energy levels are known as excited states. The excitation energy or spectral gap of an excited state with energy  $E_m$  is defined to be  $E_m - E_1$ . Physically it corresponds to the energy required to promote the electrons from the ground state to the excited state.*

Besides the quantized energy levels  $E_n$ , there exist important additional discrete quantum numbers associated with the atomic Schrödinger equation which arise from its symmetries. Their precise definition, albeit very natural, takes a little more work.

The model (1), (2), (4), (5) is invariant under

- (i) simultaneous rotation of all electron positions about the origin,  $\Psi(x_1, s_1, \dots, x_N, s_N) \mapsto \Psi(R^T x_1, s_1, \dots, R^T x_N, s_N)$ ,  $R \in SO(3)$ ;
- (ii) simultaneous rotation of all electron spins (by a unitary matrix  $U \in SU(2)$ );

(iii) simultaneous inversion of all electron positions at the origin,  $\Psi(x_1, s_1, \dots, x_N, s_N) \mapsto \Psi(-x_1, s_1, \dots, -x_N, s_N) =: \hat{R}\Psi$ .

(In group theory language, the symmetry group is  $SO(3) \times SU(2) \times \mathbb{Z}_2$ , the third factor being the inversion group consisting of  $\hat{R}$  and the identity. When  $N = 1$ , there exists an additional symmetry, which gives rise to conservation of the quantized Runge–Lenz vector; but it is broken by the interaction term in (2) when  $N \geq 2$ . Note also that even though the Hamiltonian (2) is invariant under the larger group of nonsimultaneous rotation of spins, the antisymmetry condition (5) is not.)

The conserved quantities, i.e., operators which commute with the Hamiltonian, which arise from the above symmetries are

(i)  $\mathbf{L} = \sum_{j=1}^N \mathbf{L}(j)$  (many-electron angular momentum operator);

(ii)  $\mathbf{S} = \sum_{j=1}^N \mathbf{S}(j)$  (many-electron spin operator);

(iii)  $\hat{R}$  (parity operator),

where

$$\mathbf{L}(j) = \begin{pmatrix} L_1(j) \\ L_2(j) \\ L_3(j) \end{pmatrix}, \quad \mathbf{S}(j) = \begin{pmatrix} S_1(j) \\ S_2(j) \\ S_3(j) \end{pmatrix},$$

and  $L_\alpha(j)$ ,  $S_\alpha(j)$  ( $\alpha = 1, 2, 3$ ) denote the usual angular momentum, respectively, spin operators, acting on the  $j$ th coordinate. Explicitly, on  $N$ -electron states  $\Psi(x_1, s_1, \dots, x_N, s_N)$ ,  $x_j \in \mathbb{R}^3$ ,  $s_j \in \{\pm\frac{1}{2}\}$ , and denoting  $x_j = (y^{(1)}, y^{(2)}, y^{(3)})$ ,  $L_\alpha(j)$  is the partial differential operator

$$(6) \quad L_\alpha(j) = \frac{1}{i} \left( y^{(\alpha+1)} \frac{\partial}{\partial y^{(\alpha-1)}} - y^{(\alpha-1)} \frac{\partial}{\partial y^{(\alpha+1)}} \right),$$

and  $S_\alpha(j)$  is multiplication by a Pauli matrix,

$$\begin{pmatrix} (S_\alpha(j)\Psi)(x_1, s_1, \dots, x_j, \frac{1}{2}, \dots, x_N, s_N) \\ (S_\alpha(j)\Psi)(x_1, s_1, \dots, x_j, -\frac{1}{2}, \dots, x_N, s_N) \end{pmatrix} \\ = \sigma_\alpha \begin{pmatrix} \Psi(x_1, s_1, \dots, x_j, \frac{1}{2}, \dots, x_N, s_N) \\ \Psi(x_1, s_1, \dots, x_j, -\frac{1}{2}, \dots, x_N, s_N) \end{pmatrix},$$

where the  $\sigma_\alpha$  are the Pauli matrices

$$\sigma_1 := \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 := \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 := \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The fact that the operators (i), (ii), (iii) commute with the Hamiltonian (2) can be checked by direct inspection using the above formulae, without reference to the underlying symmetry group.

The components of total angular momentum and total spin,  $L_\alpha = \sum_{j=1}^N L_\alpha(j)$  and  $S_\alpha = \sum_{j=1}^N S_\alpha(j)$ , obey the usual commutator relations

$$[L_\alpha, L_\beta] = iL_\gamma, \quad [S_\alpha, S_\beta] = iS_\gamma \quad (\alpha, \beta, \gamma \text{ cyclic}).$$

Angular momentum representation theory, together with simple considerations concerning the above specific action of the operators on  $N$ -electron states, yields the following well-known facts (see, e.g., [FriXX]).

LEMMA 2.1. (a) For arbitrary  $N$  and  $Z$ , a set of operators which commutes with the Hamiltonian  $H$  and with each other is given by

$$(7) \quad \underline{\mathbf{L}}^2, L_3, \underline{\mathbf{S}}^2, S_3, \hat{R}.$$

(b) The eigenvalues of  $\underline{\mathbf{L}}^2$ ,  $\underline{\mathbf{S}}^2$ , and  $\hat{R}$  (acting on  $L_a^2((\mathbb{R}^3 \times \mathbb{Z}_2)^N)$ ) are, respectively,

$$(8) \quad L(L+1), \quad L = 0, 1, 2, \dots,$$

$$(9) \quad S(S+1), \quad S = \begin{cases} \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots, \frac{N}{2}, & N \text{ odd,} \\ 0, 1, 2, \dots, \frac{N}{2}, & N \text{ even,} \end{cases}$$

$$(10) \quad p = \pm 1.$$

(c) For fixed  $L$ ,  $S$ , and  $p$ , on any joint eigenspace of  $H$ ,  $\underline{\mathbf{L}}^2$ ,  $\underline{\mathbf{S}}^2$ , and  $\hat{R}$ ,  $L_3$  has eigenvalues  $M = -L, -L+1, \dots, L$ , and  $S_3$  has eigenvalues  $M_S = -S, -S+1, \dots, S$ . In particular, the eigenspace has dimension greater than or equal to  $(2L+1) \cdot (2S+1)$ , with equality in the case when the joint eigenspaces of  $H$  and the operators (7) are nondegenerate (i.e., one-dimensional).

Here we have employed the usual notation  $\underline{\mathbf{L}}^2 = L_1^2 + L_2^2 + L_3^2$  (and analogously for  $\underline{\mathbf{S}}^2$ ).

From the above we see that the main differences between the symmetries of many-electron atoms and those of hydrogen are the absence of an analogon of the quantized Runge–Lenz vector and the nontrivial action of the spin operator  $\underline{\mathbf{S}}^2$  (for  $N = 1$  it is equal to the trivial operator  $\frac{3}{4}I$ ).

DEFINITION 2. The values of  $L$ ,  $S$ , and  $p$  for eigenstates of  $\underline{\mathbf{L}}^2$ ,  $\underline{\mathbf{S}}^2$ ,  $\hat{R}$  are called the total angular momentum quantum number, the total spin quantum number, and the parity of the state.

From the above lemma we see that for each energy level of  $H$  there exist unique quantum numbers  $L$ ,  $S$ ,  $p$  characterizing the symmetry of the eigenspace (except in “nongeneric” cases where the joint eigenspaces of  $H$  and the operators (7) are degenerate, in which case there exists a unique finite set of such quantum numbers). In the chemistry literature these numbers for an energy level are usually given in the form  $^{2S+1}X^\nu$ , where  $L$  corresponds to  $X$  via  $0 \rightarrow S$ ,  $1 \rightarrow P$ ,  $2 \rightarrow D$ ,  $3 \rightarrow F$ , and where no superscript  $\nu$  means  $p = 1$ , and  $\nu = o$  (for odd) stands for  $p = -1$ . For example, the carbon values  $L = 1$ ,  $S = 1$ ,  $p = 1$  from Table 1 would be denoted  $^3P$ , and the nitrogen values  $L = 0$ ,  $S = 3/2$ ,  $p = -1$  by  $^4S^o$ .

Of particular physical and chemical interest is the energetic ordering in which different combinations of  $L$  and  $S$  appear in the spectrum of the Hamiltonian (2); see section 7.

**3. Ground states of the first ten atoms in the large  $Z$  limit.** We are now in a position to state a principal result of this paper.

*Notation.*  $|\eta_1 \dots \eta_N\rangle$  denotes the Slater determinant (or antisymmetrized tensor product) of the orbitals  $\eta_j \in L^2(\mathbb{R}^3 \times \mathbb{Z}_2)$ ,  $|\eta_1 \dots \eta_N\rangle(x_1, s_1, \dots, x_N, s_N) = (N!)^{-1/2} \det(\eta_i(x_j, s_j))_{i,j=1}^N$ .  $\phi \uparrow$ ,  $\phi \downarrow$  stands for the spin-up and spin-down orbitals  $\phi(x)\delta_{\pm 1/2}(s) \in L^2(\mathbb{R}^3 \times \mathbb{Z}_2)$ . For a linear operator on the  $N$ -electron Hilbert space (3),  $\|A\|$  denotes the usual operator norm  $\sup\{\|A\Psi\| : \Psi \in L_a^2((\mathbb{R}^3 \times \mathbb{Z}_2)^N), \|\Psi\| = 1\}$ .

THEOREM 3.1. Consider the atomic Schrödinger equation (1), (2), (3) for the atom/ion with  $N = 1$  to 10 electrons and nuclear charge  $Z$ .

(i) For sufficiently large  $Z$ , the ground state has the spin and angular momentum quantum number  $S$ ,  $L$  and the dimension given in Table 1.

(ii) In the limit  $Z \rightarrow \infty$ , the ground state is asymptotic to the explicit vector space given in Table 2, in the sense that the projection operators  $P_0, \tilde{P}_0$  onto these spaces satisfy  $\lim_{Z \rightarrow \infty} \|P_0 - \tilde{P}_0\| = 0$ . Here 1, 2, 3, 4, 5 stand for the scaled hydrogen orbitals (mathematically: hypergeometric functions)  $\phi_{1s} \uparrow, \phi_{2s} \uparrow, \phi_{2p_3} \uparrow, \phi_{2p_1} \uparrow, \phi_{2p_2} \uparrow$  from (24), (25), and  $\bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{5}$  denote the corresponding spin-down orbitals.

TABLE 2

Ground states of the atomic Schrödinger equation in the limit  $Z \rightarrow \infty$ . The indicated wave functions are an orthonormal basis of the ground state. See Theorem 3.1 for notation. The symmetry agrees with experiment for each sequence and all  $Z$ .

Isoelectronic sequence	Symmetry	Ground state	Dimension
H	$^2S$	$ 1\rangle,  \bar{1}\rangle$	2
He	$^1S$	$ \bar{1}\bar{1}\rangle$	1
Li	$^2S$	$ \bar{1}\bar{1}\bar{2}\rangle,  \bar{1}\bar{1}\bar{2}\rangle$	2
Be	$^1S$	$\frac{1}{\sqrt{1+c^2}}( \bar{1}\bar{1}\bar{2}\bar{2}\rangle + c\frac{1}{\sqrt{3}}( \bar{1}\bar{1}\bar{3}\bar{3}\rangle +  \bar{1}\bar{1}\bar{4}\bar{4}\rangle +  \bar{1}\bar{1}\bar{5}\bar{5}\rangle))$ $c = -\frac{\sqrt{3}}{59049}(2\sqrt{1509308377} - 69821) = -0.2310996 \dots$	1
B	$^2P^o$	$\frac{1}{\sqrt{1+c^2}}( \bar{1}\bar{1}\bar{2}\bar{2}i\rangle + c\frac{1}{\sqrt{2}}( \bar{1}\bar{1}\bar{i}j\bar{j}\rangle +  \bar{1}\bar{1}\bar{i}k\bar{k}\rangle))$ $\frac{1}{\sqrt{1+c^2}}( \bar{1}\bar{1}\bar{2}\bar{2}i\rangle + c\frac{1}{\sqrt{2}}( \bar{1}\bar{1}\bar{i}j\bar{j}\rangle +  \bar{1}\bar{1}\bar{i}k\bar{k}\rangle))$ $(i, j, k) = (3, 4, 5), (4, 5, 3), (5, 3, 4)$ $c = -\frac{\sqrt{2}}{393660}(\sqrt{733174301809} - 809747) = -0.1670823 \dots$	6
C	$^3P$	$\frac{1}{\sqrt{1+c^2}}( \bar{1}\bar{1}\bar{2}\bar{2}ij\rangle + c \bar{1}\bar{1}\bar{k}\bar{k}i\bar{j}\rangle)$ $\frac{1}{\sqrt{1+c^2}}(\frac{1}{\sqrt{2}}( \bar{1}\bar{1}\bar{2}\bar{2}i\bar{j}\rangle +  \bar{1}\bar{1}\bar{2}\bar{2}ij\rangle) + c\frac{1}{\sqrt{2}}( \bar{1}\bar{1}\bar{k}\bar{k}i\bar{j}\rangle +  \bar{1}\bar{1}\bar{k}\bar{k}ij\rangle))$ $\frac{1}{\sqrt{1+c^2}}( \bar{1}\bar{1}\bar{2}\bar{2}i\bar{j}\rangle + c \bar{1}\bar{1}\bar{k}\bar{k}i\bar{j}\rangle)$ $(i, j, k) = (3, 4, 5), (4, 5, 3), (5, 3, 4)$ $c = -\frac{1}{98415}(\sqrt{221876564389} - 460642) = -0.1056318 \dots$	9
N	$^4S^o$	$ \bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{4}\bar{5}\rangle$ $\frac{1}{\sqrt{3}}( \bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{4}\bar{5}\rangle +  \bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{4}\bar{5}\rangle +  \bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{4}\bar{5}\rangle)$ $\frac{1}{\sqrt{3}}( \bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{4}\bar{5}\rangle +  \bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{4}\bar{5}\rangle +  \bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{4}\bar{5}\rangle)$ $ \bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{4}\bar{5}\rangle$	4
O	$^3P$	$ \bar{1}\bar{1}\bar{2}\bar{2}i\bar{j}k\rangle$ $\frac{1}{\sqrt{2}}( \bar{1}\bar{1}\bar{2}\bar{2}i\bar{j}k\rangle +  \bar{1}\bar{1}\bar{2}\bar{2}i\bar{j}k\rangle)$ $ \bar{1}\bar{1}\bar{2}\bar{2}i\bar{j}k\rangle$ $(i, j, k) = (3, 4, 5), (4, 5, 3), (5, 3, 4)$	9
F	$^2P^o$	$ \bar{1}\bar{1}\bar{2}\bar{2}i\bar{j}j\bar{k}\rangle$ $ \bar{1}\bar{1}\bar{2}\bar{2}i\bar{j}j\bar{k}\rangle$ $(i, j, k) = (3, 4, 5), (4, 5, 3), (5, 3, 4)$	6
Ne	$^1S$	$ \bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{3}\bar{4}\bar{4}\bar{5}\bar{5}\rangle$	1

In fact, all low-lying energy levels and eigenstates can be determined exactly in the above limit. See Theorem 7.1. Note also that, as we will see below, the asymptotic ground states in the table are the exact ground states of the limit model (16), (17) and become  $Z$ -independent after the rescaling (11).

The derivation of these results requires five steps:

1. Reduction to the finite-dimensional problem  $PHP\Psi = E\Psi, \Psi \in V_0(N)$ , described in (16), (17).
2. Explicit determination of  $V_0(N)$ .



3. Choice of a suitable basis of  $V_0(N)$  making  $PHP$  particularly simple.
4. Explicit determination of the  $d \times d$  (i.e., in the case of carbon,  $70 \times 70$ ) matrix representing the Hamiltonian  $PHP$  from (16) in this basis.
5. Spectral analysis of this matrix.

These steps are carried out in sections 4, 5, 6.3, 6.4–6.6, and 7. Steps 1 and 2 follow from standard perturbation theory, respectively, hydrogen atom theory. Step 3 is achieved by a basis adapted to the symmetries of  $PHP$  (see Lemma 2.1) leading to block diagonal structure. Step 4 exploits, in addition, the fact that the Hamiltonian contains only one-body and two-body terms, allowing one to reduce evaluation of the required  $N$ -electron matrix elements  $\langle \Psi | H | \tilde{\Psi} \rangle$ , which are integrals over  $\mathbb{R}^{3N}$ , to one- and two-electron matrix elements.

**3.1. Comparison with the semiempirical Bohr–Hund–Slater picture of the periodic table.** The result of Theorem 3.1 provides a mathematical justification of the semiempirical “Aufbau principle” (from the German word for building up) developed notably by Bohr, Hund, and Slater to explain the periodic table [Boh22, Hun25, LL77, Sch01, AdP01]. The Aufbau principle is based on three semiempirical postulates:

- (a) Each electron in an atom occupies a hydrogenic orbital.<sup>1</sup>
- (b) *Subshell ordering.* The orbitals in each hydrogen energy level, or shell, form subshells which are occupied in the order  $1s \ 2s \ 2p \ 3s \ 3p \ 4s \ 3d \ \dots$
- (c) *Hund’s rule.* Within any partially filled subshell, the electrons adopt a configuration with the greatest possible number of aligned spins.

Thus, for example, in carbon the six electrons would occupy the orbitals  $1s \uparrow \ 1s \downarrow \ 2s \uparrow \ 2s \downarrow \ 2p_1 \uparrow \ 2p_2 \uparrow$  (note that the alternative choices  $2p_1 \downarrow$  or  $2p_2 \downarrow$  for the last orbital would be consistent with (b) but not (c)).

This beautiful heuristic picture is seen to emerge in Theorem 3.1 in a natural way, without reliance on the above nontrivial postulates or numerical simulations (up to small but interesting corrections).

(i) For seven out of ten elements (H, He, Li, N, O, F, Ne), the Aufbau principle configuration (when interpreted not as a collection of individual electronic states, but as a Slater-determinantal many-electron wavefunction) is an element of the asymptotic Schrödinger ground state.

(ii) For the remaining three elements (Be, B, C), the Aufbau principle configuration is the dominant part of an element of the asymptotic Schrödinger ground state.

The following are corrections to the semiempirical rules emerging in the large  $Z$  limit of quantum mechanics:

(1) Alongside any Slater determinant, the asymptotic ground state contains its orbit under the symmetry group of the many-electron Schrödinger equation (see Lemma 2.1).

(2) The corrections to the Aufbau principle configurations in (ii) come from different subshells, indicating that rule (b) is not strictly obeyed. We term this effect, which does not seem to have received mathematical attention,  **$2s^2$ – $2p^2$  resonances**: besides the Aufbau principle configurations  $1s^2 2s^2$ ,  $1s^2 2s^2 2p$ , and  $1s^2 2s^2 2p^2$ , a significant percentage is also present of, respectively,  $1s^2 2p^2$ ,  $1s^2 2p^3$ , and  $1s^2 2p^4$ . This could be described as a resonance of the standard configuration with a configuration

<sup>1</sup>In fact, in Bohr’s and Hund’s original works [Boh22, Hun25], which narrowly predate the Schrödinger equation, the electrons were supposed to occupy hydrogenic Bohr orbits.

in which the two  $2s$  orbitals have been substituted by two  $2p$  orbitals. Why this phenomenon occurs only for Be, B, C has a simple group-theoretic reason: Tables 12, 13 show that such a substitution which preserves the total quantum numbers  $L$  and  $S$  is possible only in these three cases.

(3) For excited states, Hund's rules are in rare cases found to disagree with the experimental and mathematical results; see section 8.

**3.2. Comparison with other approaches.** First we comment on the asymptotic regime in which the above picture emerges, namely,  $N$  fixed,  $Z \rightarrow \infty$ . These parameters are the only ones contained in the electronic Schrödinger equation that can be varied in ground states of a physical system. To capture chemical specificity,  $N$  must be kept fixed. A priori,  $Z$  could be made either small or large; but making it small leads to nonexistence of bound electrons [Lie84]. This leaves  $Z \rightarrow \infty$ , i.e., the limit studied above, as the only option.

This limit has attracted considerable previous attention in the physics and chemistry literature in connection with asymptotic expansions of energies and numerical evaluation of the coefficients. See section 4 and the references given there. But we do not know of any effort to derive a numerical analogue of Table 2 in this way (which would correspond to truncating the expansion at first order in  $1/Z$ ; see Theorem 4.1), even though, in principle, the tools to do so were available. In fact, in the only case we are aware of where first order wavefunctions are given [Lay59, Table 1, p. 288], those for Be, B, C are incorrect (the standard Aufbau principle configurations are given, instead of the correlated states in Table 2).

Another interesting strategy would be to vary mathematical parameters in the Schrödinger equation which cannot be varied physically, such as  $\hbar \rightarrow 0$  (semiclassical limit), or  $D \rightarrow \infty$ , where  $D$  is the dimensionality of single-particle state space. Despite interesting results (see, e.g., the semiclassical picture of highly excited states of helium in [TRR00], and the total atomic energies in [Loe86] via large- $D$  asymptotics [Wit80, Her86]), these ideas have so far not been aimed at, or led to, explanations of the main features of the periodic table.

The large majority of the literature on atomic systems is computational and does not take the Schrödinger equation, but various simplified models as a starting point. Explanations of the filling order (postulate (b) above) in terms of numerical solutions of the Hartree and Hartree–Fock equations began with the pioneering work of Hartree on rubidium [Har28]; for treatments of large classes of atoms, see, e.g., [Har57, FF77, TTST94]. Note that these models assume a significant part of postulate (a) from the outset, namely, that electrons occupy individual orbitals and that these have  $1s$ ,  $2s$ ,  $2p$ , etc., symmetry. The asymptotic Schrödinger ground states which we determined above beautifully illustrate both the power of the Slater determinant ansatz in Hartree–Fock theory and its limitations: in several cases other than noble gases the ground state contains a determinantal state, but for some of the atoms it does not.

Finally we remark that the refined, multiconfigurational methods developed in quantum chemistry (see, e.g., [FF77, BT86, SO96]) assume, on a somewhat ad hoc basis, exactly the structure of the wavefunctions which emerges naturally in Table 2, namely, finite linear combinations of Slater determinants. The only reason preventing these methods from being asymptotically exact within numerical error as  $Z \rightarrow \infty$  is the use of Gaussians to represent the orbitals (see our companion paper [FG09]).

**4. Reduction to the perturbation theory model.** The first step in establishing the above result is to show that (1) simplifies to a finite-dimensional model in

the limit of fixed electron number  $N$  and large nuclear charge  $Z$ .

If  $\Psi$  solves the original Schrödinger equation (1), then an elementary calculation shows that its rescaling

$$(11) \quad \tilde{\Psi}(x_1, s_1, \dots, x_N, s_N) = Z^{-3N/2} \Psi(Z^{-1}x_1, s_1, \dots, Z^{-1}x_N, s_N)$$

solves the equation

$$(12) \quad \left( \tilde{H}_0 + \frac{1}{Z} V_{ee} \right) \tilde{\Psi} = \tilde{E} \tilde{\Psi},$$

where  $\tilde{H}_0$  is the  $Z$ -independent Hamiltonian

$$(13) \quad \tilde{H}_0 = \sum_{i=1}^N \left( -\frac{1}{2} \Delta_{x_i} - \frac{1}{|x_i|} \right)$$

(acting on the  $N$ -electron Hilbert space (3)) and  $\tilde{E} = \frac{1}{Z^2} E$ . The elementary but important observation now is that the interaction term  $\frac{1}{Z} V_{ee}$  in (12) becomes small if  $Z$  is large, allowing us to treat the interaction by perturbation theory.

Let us first derive the ensuing perturbation-theoretic model informally, then formulate a theorem. By the first order Rayleigh–Schrödinger perturbation theory, (12) is expected to be well approximated by

$$(14) \quad \tilde{P}(\tilde{H}_0 + \frac{1}{Z} V_{ee}) \tilde{P} \tilde{\Psi} = \tilde{E} \tilde{\Psi}, \quad \tilde{\Psi} \in \tilde{V}_0, \quad \tilde{P} = \text{orth. projector onto } \tilde{V}_0,$$

$$(15) \quad \tilde{V}_0 = \text{ground state eigenspace of } \tilde{H}_0,$$

with  $\tilde{H}_0$  as in (13). Now we undo the rescaling (11). This yields the model

$$(16) \quad PHP\Psi = E\Psi, \quad \Psi \in V_0, \quad P = \text{orth. projector onto } V_0,$$

$$(17) \quad V_0 = \text{ground state eigenspace of } H_0, \quad H_0 = \sum_{i=1}^N \left( -\frac{1}{2} \Delta_{x_i} - \frac{Z}{|x_i|} \right),$$

where  $H$  is the original Hamiltonian (2).

We call (16), (17) the *PT model*. While it is still a fully interacting quantum many-body model, the key simplification is that the space  $V_0$  is finite-dimensional. Its dimension for different atoms is easily read off from Lemma 5.1 below.

TABLE 3  
Dimensions of degenerate  $H_0$  ground states, as given by Lemma 5.1.

Atom	He	Li	Be	B	C	N	O	F	Ne
$N$	2	3	4	5	6	7	8	9	10
$\dim V_0$	1	8	28	56	70	56	28	8	1

An important feature of the PT model is that it retains the full symmetries of the atomic Schrödinger equation.

LEMMA 4.1. *For arbitrary  $N$  and  $Z$ , with  $P$  as defined above and with  $H$  denoting the Hamiltonian (2), the operators (7)*

- (i) *leave the ground state  $V_0$  of  $H_0$  invariant;*
- (ii) *commute with the PT Hamiltonian  $PHP : V_0 \rightarrow V_0$ .*

*Proof.* By direct inspection the operators (7) commute with  $H_0$ . Since  $V_0$  is an eigenspace of  $H_0$ , they must therefore leave  $V_0$  invariant, and commute with the projector  $P$  onto  $V_0$ . As already shown (see Lemma 2.1), the operators (7) also commute with  $H$ , and hence with the composition  $PHP$ .

We now come to the rigorous justification of the PT model (16), (17).

**THEOREM 4.1.** *Let  $N = 1, \dots, 10$ ,  $Z > 0$ , and let  $n(N)$  be the number of energy levels of the PT model (16), (17). Then the following hold:*

(a) *For all sufficiently large  $Z$ , the lowest  $n(N)$  energy levels  $E_1(N, Z) < \dots < E_{n(N)}(N, Z)$  of the full Hamiltonian (2) have exactly the same dimension, total spin quantum number, total angular momentum quantum number, and parity as the corresponding PT energy levels  $E_1^{PT}(N, Z) < \dots < E_{n(N)}^{PT}(N, Z)$ .*

(b) *The lowest  $n(N)$  energy levels of the full Hamiltonian have the asymptotic expansion*

$$\frac{E_j(N, Z)}{Z^2} = \frac{E_j^{PT}(N, Z)}{Z^2} + O\left(\frac{1}{Z^2}\right) = \tilde{E}^{(0)} + \frac{1}{Z}\tilde{E}_j^{(1)} + O\left(\frac{1}{Z^2}\right) \text{ as } Z \rightarrow \infty,$$

where  $\tilde{E}^{(0)}$  is the lowest eigenvalue of  $\tilde{H}_0$  and the  $\tilde{E}_j^{(1)}$  are the energy levels of  $\tilde{P}V_{ee}\tilde{P}$  on  $\tilde{V}_0$ .

(c) *The projectors  $P_1, \dots, P_{n(N)}$  onto the lowest  $n(N)$  eigenspaces of the full Hamiltonian satisfy*

$$\|P_j - P_j^{PT}\| \rightarrow 0 \text{ as } Z \rightarrow \infty,$$

where the  $P_j^{PT}$  are the corresponding projectors for the PT model.

The idea that for large  $Z$  the interelectron term  $\tilde{E}_j^{(1)}$  provides the first order correction to the noninteracting energy is well known in the physics literature (see, e.g., [Hy130, BS57, SC62, SW67, RD71, Wil84], which treats nondegenerate eigenvalues, and see [Lay59], which gives an expansion similar to that in (b), not accounting for multiplicities, and numerical tables of  $\tilde{E}_j^{(1)}$  in the degenerate case). The main new insight here is the absence of further splittings at higher orders of perturbation theory (see statement (a) in the theorem). This is remarkable, considering that it fails in the simple  $3 \times 3$  matrix example

$$H(\epsilon) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \epsilon \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The eigenvalues are  $\sqrt{1 + \epsilon^2}$ ,  $1$ ,  $-\sqrt{1 + \epsilon^2}$ , and hence nondegenerate for  $\epsilon \neq 0$ , but the leading eigenvalue is degenerate in first order perturbation theory.

*Proof.* Let  $\tilde{E}_1^{PT} < \dots < \tilde{E}_{n(N)}^{PT}$  be the energy levels of the scaled model (14), (15), and let  $d_j, \tilde{P}_j^{PT}$  be the corresponding eigenspace dimensions and eigenspace projectors. By perturbation theory for relatively bounded perturbations of self-adjoint operators (see, e.g., [Kat95, FriXX]), exactly  $d_j$  eigenvalues of the scaled Schrödinger equation (12) including multiplicity are asymptotic to first order in  $1/Z$  to the  $j$ th eigenvalue of (16), (17). More precisely: The lowest  $d_1 + \dots + d_{n(N)}$  eigenvalues of (12) including multiplicity, labeled  $\tilde{E}_{j,k}$ ,  $j = 1, \dots, n(N)$ ,  $k = 1, \dots, d_j$ ,  $\tilde{E}_{1,1} \leq \dots \leq \tilde{E}_{1,d_1} \leq \tilde{E}_{2,1} \leq \dots \leq \tilde{E}_{2,d_2} \leq \dots$ , satisfy

$$\tilde{E}_{j,k} = \tilde{E}^{(0)} + \frac{1}{Z}\tilde{E}_j^{(1)} + O\left(\frac{1}{Z^2}\right) \text{ as } Z \rightarrow \infty, \quad k = 1, \dots, d_j.$$

Moreover the projector  $\tilde{P}_j$  onto the span of these  $d_j$  eigenstates satisfies

$$(18) \quad \|\tilde{P}_j - \tilde{P}_j^{PT}\| \rightarrow 0 \text{ as } Z \rightarrow \infty.$$

Next, we investigate the Schrödinger eigenspace dimensions. By Lemma 4.1, each PT eigenspace possesses well-defined spin, angular momentum, and parity quantum numbers  $L$ ,  $S$ , and  $p$ , and by inspection of the explicit formulae in Theorem 7.1 below, the space has minimal dimension subject to these numbers. On the other hand, by (18), for sufficiently large  $Z$  these numbers must agree with those of the eigenspaces of (12); hence by Lemma 2.1 (c),  $\tilde{E}_{j,1} = \dots = \tilde{E}_{j,d_j}$ . Note that without the information on minimality of the PT dimensions, we would not be able to exclude the possibility of further splittings of the Schrödinger eigenvalues beyond the PT splittings, at higher orders of perturbation theory; this is the only reason the restriction  $N \leq 10$  is needed.

The theorem now follows by applying the isometric scaling transformation (11).

**5. State space of the PT model.** The important starting point for solving the PT model is the fact that its state space, the ground state of  $H_0$ , can be determined explicitly. This will follow from the exact solubility of the Schrödinger equation of hydrogen and basic many-body arguments. To explain these matters, we start from the hydrogen atom Hamiltonian

$$(19) \quad h = -\frac{1}{2}\Delta - \frac{Z}{|x|},$$

$x \in \mathbb{R}^3$ , acting on  $L^2(\mathbb{R}^3 \times \mathbb{Z}_2)$ . For hydrogen,  $Z = 1$ , but the parameter  $Z > 0$  will be useful later. Its eigenvalues are given by (see, e.g., [Gri95])

$$(20) \quad e_n = -\frac{Z^2}{2n^2}, \quad n \in \mathbb{N},$$

and have corresponding  $2n^2$ -dimensional eigenspaces with orthonormal basis

$$(21) \quad \mathcal{B}_n = \{\phi_{n\ell m s}(x, s) \mid \ell = 0, \dots, n-1, m = -\ell, -\ell+1, \dots, \ell, s = -\frac{1}{2}, \frac{1}{2}\},$$

where  $\phi_{n\ell m s} \in L^2(\mathbb{R}^3 \times \mathbb{Z}_2)$  is, up to normalization, the unique eigenfunction of  $h$ ,  $\underline{L}^2$ ,  $L_3$ , and  $S_3$  with eigenvalues  $-Z^2/(2n^2)$ ,  $\ell(\ell+1)$ ,  $m$ , and  $s$ , respectively.

Later, it will be useful to have an explicit form for these so-called hydrogen orbitals, which in polar coordinates with spin coordinate  $s \in \mathbb{Z}_2$  are given by

$$(22) \quad \phi_{n,\ell,m,\sigma}(r, \theta, \phi, s) = \phi_{n\ell m}(r, \theta, \phi)\delta_\sigma(s) = Z^{3/2}R_{n,\ell}(Zr)Y_{\ell,m}(\theta, \phi)\delta_\sigma(s),$$

where

$$(23) \quad R_{n,\ell}(r) := \left( \left( \frac{2}{n} \right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]} \right)^{1/2} e^{-r/n} \left( \frac{2r}{n} \right)^\ell L_{n-\ell-1}^{2\ell+1} \left( \frac{2r}{n} \right).$$

Here  $L_n^k(x)$  is a generalized Laguerre polynomial and  $Y_{\ell,m}(\theta, \phi)$  is a spherical harmonic [AS72]. In cartesian coordinates, the  $n = 1$  and  $n = 2$  orbitals are

$$\begin{aligned}
 \phi_{1,0,0}(x) &= \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Z|x|} =: \phi_{1s}(x), \\
 \phi_{2,0,0}(x) &= \frac{Z^{3/2}}{\sqrt{8\pi}} \left(1 - \frac{Z|x|}{2}\right) e^{-Z|x|/2} =: \phi_{2s}(x), \\
 \phi_{2,1,0}(x) &= \frac{Z^{5/2}}{\sqrt{32\pi}} x_3 e^{-Z|x|/2} =: \phi_{2p_3}, \\
 \phi_{2,1,\pm 1}(x) &= \frac{Z^{5/2}}{\sqrt{32\pi}} \frac{x_1 \pm ix_2}{\sqrt{2}} e^{-Z|x|/2} =: \phi_{2p_{\pm}}.
 \end{aligned}
 \tag{24}$$

Often, it is convenient to work with—instead of the last two functions—their real linear combinations:

$$\frac{Z^{5/2}}{\sqrt{32\pi}} x_j e^{-Z|x|/2} =: \phi_{2p_j}(x), \quad j = 1, 2.
 \tag{25}$$

The following lemma describes how the eigenfunctions for the noninteracting many-electron system are formed from these one-electron eigenfunctions.

LEMMA 5.1 (standard “folklore”; see [FriXX] for a rigorous proof). (a) *The lowest eigenvalue of the operator*

$$H_0 := -\frac{1}{2} \sum_{i=1}^N \Delta_i - \sum_{i=1}^N \frac{Z}{|x_i|}$$

on the space  $L_a^2((\mathbb{R}^3 \times \mathbb{Z}_2)^N)$  of square-integrable functions  $\Psi : (\mathbb{R}^3 \times \mathbb{Z}_2)^N \rightarrow \mathbb{C}$  satisfying the antisymmetry condition (5) is  $E = \sum_{n=1}^N \tilde{e}_n$ , where  $\tilde{e}_1 \leq \tilde{e}_2 \leq \dots$  is an ordered list including multiplicity of the hydrogen eigenvalues (20).

(b) *The corresponding eigenspace is*

$$\begin{aligned}
 V_0 = \text{Span} \left\{ \left| \chi_1 \dots \chi_{d_*} \psi_{i_1} \dots \psi_{i_{N-d_*}} \right| \right. \\
 \left. 1 \leq i_1 < \dots < i_{N-d_*} \leq 2(n_* + 1)^2 \right\},
 \end{aligned}
 \tag{26}$$

where the functions  $\chi_i$  and  $\psi_i$  (“core orbitals” and “valence orbitals”) and the integers  $d_*$  and  $n_*$  (“number of core orbitals” and “number of closed shells”) are defined as follows:  $d_*(N)$  is the largest number of form  $\sum_{j=1}^n 2j^2$  which is less than or equal to  $N$ ,  $n_*(N)$  is the corresponding value of  $n$ ,

$$\{\chi_1, \dots, \chi_{d_*}\} = \mathcal{B}_1 \cup \dots \cup \mathcal{B}_{n_*}$$

(union of the orthonormal bases (21) of the first  $n_*$  hydrogen eigenspaces), and

$$\{\psi_1, \dots, \psi_{2(n_*+1)^2}\} = \mathcal{B}_{n_*+1}$$

(orthonormal basis of the  $(n_* + 1)$ st hydrogen eigenspace).

Thus the ground state of the noninteracting Hamiltonian is spanned by Slater determinants (alias antisymmetrized tensor products) formed from scaled hydrogen orbitals, “filled” in order of increasing one-electron energy.

Due to the freedom of choosing any  $N - d_*$  eigenfunctions  $\psi_i$  (“valence orbitals”) from the basis of the highest relevant hydrogen eigenspace, whose dimension is  $2(n_* + 1)^2$ , the noninteracting ground state has typically a large degeneracy:

$$(27) \quad d_0 := \text{dimension of the ground state } H_0 = \binom{2(n_*(N) + 1)^2}{N - d_*(N)}.$$

**Specialization to the second row atoms and their isoelectronic ions** ( $N = 3, \dots, 10$ ). In this case, the number  $d_*$  of core orbitals equals 2, the number  $n_*$  of closed shells equals 1, and the dimension  $2(n_* + 1)^2$  of the hydrogen eigenspace from which the valence orbitals are selected equals 8. Thus by (27), the dimension of the ground state equals

$$d_0 = \binom{8}{N - 2}.$$

These numbers are given in Table 3. The set of core, respectively, valence, orbitals is (using the real orbitals  $\phi_{2p_1}, \phi_{2p_2}$  instead of  $\phi_{2p_\pm}$ )

$$(28) \quad \{\chi_1, \chi_2\} = \{\phi_{1s} \uparrow, \phi_{1s} \downarrow\},$$

$$(29) \quad \{\psi_1, \dots, \psi_8\} = \{\phi_{2s} \uparrow, \phi_{2s} \downarrow, \phi_{2p_1} \uparrow, \phi_{2p_1} \downarrow, \phi_{2p_2} \uparrow, \phi_{2p_2} \downarrow, \phi_{2p_3} \uparrow, \phi_{2p_3} \downarrow\}.$$

Here we have employed the standard notation  $\phi \uparrow, \phi \downarrow$  for the two spin orbitals  $\phi(x)\delta_{\pm 1/2}(\sigma)$ .

Finally, the ground state of  $H_0$  is

$$(30) \quad V_0(N) = \text{Span} \left\{ |\chi_1 \chi_2 \psi_{i_1} \dots \psi_{i_{N-2}} \rangle \mid 1 \leq i_1 < \dots < i_{N-2} \leq 8 \right\}.$$

**6. Determining the matrix PHP.** In this section we determine explicitly the Hamiltonian matrices *PHP* for all second period atoms.

Most of our arguments do not rely on the special radial form of the hydrogen orbitals (28), (29) appearing in the definition of the subspace  $V_0(N)$ . Hence in this section, unless stated otherwise,  $V_0(N)$  denotes the space (30), (28), (29) with the more general orbitals

$$(31) \quad \varphi_{1s}(x) = R_1(|x|), \quad \varphi_{2s}(x) = R_2(|x|), \quad \varphi_{2p_i}(x) = R_3(|x|)x_i \quad (i = 1, 2, 3),$$

where the  $\varphi$ 's are in  $L^2(\mathbb{R}^3)$  with norm one,  $R_i : \mathbb{R} \rightarrow \mathbb{R}$ , and  $\int_0^\infty R_1(r)R_2(r)r^2 dr = 0$ .

**6.1. Spin and angular momentum calculus on Slater determinants.** The action of the spin and angular momentum operators on  $V_0(N)$  can be calculated from their action on the orbitals (28) and (29), together with the following simple identities for the action of linear operators of form:

$$B = \sum_{i=1}^N b(i), \quad B^2 = \sum_{i,j=1}^N b(i)b(j)$$

on Slater determinants, where  $b$  is a linear operator on  $L^2(\mathbb{R}^3 \times \mathbb{Z}_2)$ :

$$(32) \quad B|\chi_1, \dots, \chi_N\rangle = \sum_{i=1}^N |\chi_1, \dots, b\chi_i, \dots, \chi_N\rangle,$$

$$(33) \quad \begin{aligned} B^2|\chi_1, \dots, \chi_N\rangle &= \sum_{i=1}^N |\chi_1, \dots, b^2\chi_i, \dots, \chi_N\rangle \\ &+ 2 \sum_{1 \leq i < j \leq N} |\chi_1, \dots, b\chi_i, \dots, b\chi_j, \dots, \chi_N\rangle. \end{aligned}$$

Direct calculations show that, for any two spatial orbitals  $\psi, \phi \in L^2(\mathbb{R}^3)$ , and orthogonal spin states  $\alpha, \beta : \mathbb{Z}_2 \rightarrow \mathbb{C}$ ,

$$\begin{aligned} \underline{S} \cdot \underline{S}\psi\alpha &= \frac{3}{4}\psi\alpha, \\ (\underline{S}(1) \cdot \underline{S}(2))\psi\alpha \otimes \phi\beta &= \frac{1}{2}\psi\beta \otimes \phi\alpha - \frac{1}{4}\psi\alpha \otimes \phi\beta, \\ (\underline{S}(1) \cdot \underline{S}(2))\psi\alpha \otimes \phi\alpha &= \frac{1}{4}\psi\alpha \otimes \phi\alpha. \end{aligned}$$

In particular, by (32) and (33),  $S_3|\psi\alpha\psi\beta\rangle = 0$  and  $\underline{S}^2|\psi\alpha\psi\beta\rangle = (\frac{3}{4} + \frac{3}{4})|\psi\alpha\psi\beta\rangle - 2 \cdot \frac{3}{4}|\psi\alpha\psi\beta\rangle = 0$ .

The angular momentum operators (6) act on the orbitals (31) as follows, independently of the choice of spin  $\alpha : \mathbb{Z}_2 \rightarrow \mathbb{C}$ :

$$\begin{aligned} L_j\varphi_{1s}\alpha &= L_j\varphi_{2s}\alpha = L_j\varphi_{2p_j}\alpha = 0, \\ L_{j+1}\varphi_{2p_j}\alpha &= -i\varphi_{2p_{j-1}}\alpha, \quad L_{j-1}\varphi_{2p_j}\alpha = i\varphi_{2p_{j+1}}\alpha, \quad j = 1, 2, 3, \end{aligned}$$

where the indices are understood modulo three. Hence we need only consider the action of  $\underline{L}^2$  on  $\varphi_{2p_i}$ , giving, for any two spin states  $\alpha$  and  $\beta$ , and  $i \neq j$ ,

$$\begin{aligned} \underline{L} \cdot \underline{L}\varphi_{2p_i}\alpha &= 2\varphi_{2p_i}\alpha, \\ (\underline{L}(1) \cdot \underline{L}(2))\varphi_{2p_i}\alpha \otimes \varphi_{2p_i}\beta &= -(\varphi_{2p_{i-1}}\alpha \otimes \varphi_{2p_{i-1}}\beta + \varphi_{2p_{i+1}}\alpha \otimes \varphi_{2p_{i+1}}\beta), \\ (\underline{L}(1) \cdot \underline{L}(2))\varphi_{2p_i}\alpha \otimes \varphi_{2p_j}\beta &= \varphi_{2p_j}\alpha \otimes \varphi_{2p_i}\beta. \end{aligned}$$

Finally we see that, for any spin state  $\alpha$ ,  $\hat{R}\varphi_{1s}\alpha = \varphi_{1s}\alpha$ ,  $\hat{R}\varphi_{2s}\alpha = \varphi_{2s}\alpha$ , and  $\hat{R}\varphi_{2p_i}\alpha = -\varphi_{2p_i}\alpha$ ,  $i = 1, 2, 3$ .

A useful and well-known consequence of the above is that the pair of  $1s$  orbitals makes no contribution to spin, angular momentum, and parity on the space (30). We state this more precisely in the following lemma.

LEMMA 6.1 (see [FriXX]). *The matrix of any of the operators (7) on  $V_0(N)$  with respect to the basis (30) is the same as that on the corresponding fewer-particle space obtained by deleting the orbitals  $\chi_1, \chi_2$ , with respect to the corresponding basis  $\{|\psi_{i_1} \dots \psi_{i_{N-2}}\rangle \mid 1 \leq i_1 < \dots < i_{N-2} \leq 8\}$ .*

**6.2. Particle-hole duality.** A further observation that simplifies the calculation of the eigenfunctions is a particle-hole duality result. We introduce a dual operator, in the spirit of the Hodge star operator from differential geometry (see, e.g., [Jos02]), as follows.

DEFINITION. *The dual of  $\alpha|\Psi\rangle$ , with*

$$|\Psi\rangle = |\varphi_{1s} \uparrow \varphi_{1s} \downarrow \psi_{i_1} \dots \psi_{i_{N-2}}\rangle$$



being any element of the basis (30) and  $\alpha \in \mathbb{C}$ , denoted by  $\ast(\alpha|\Psi\rangle)$ , is given by

$$(34) \quad \ast(\alpha|\Psi\rangle) := \alpha \ast a(\psi_{i_{N-2}}) \dots a(\psi_{i_1})|\mathbb{1}\rangle,$$

where

$$|\mathbb{1}\rangle := |\varphi_{1s} \uparrow \varphi_{1s} \downarrow \varphi_{2s} \uparrow \varphi_{2s} \downarrow \varphi_{2p_1} \uparrow \varphi_{2p_1} \downarrow \varphi_{2p_2} \uparrow \varphi_{2p_2} \downarrow \varphi_{2p_3} \uparrow \varphi_{2p_3} \downarrow\rangle$$

and  $a(\psi)$  is the usual annihilation operator which maps  $|\psi \psi_{i_1} \dots \psi_{i_k}\rangle$  to  $|\psi_{i_1} \dots \psi_{i_k}\rangle$ .

We extend  $\ast$  linearly to real linear combinations of the  $\alpha|\Psi\rangle$ , thereby obtaining an antilinear map from  $V_0(N)$  to  $V_0(10 - (N - 2))$ . We then have the following result.

LEMMA 6.2. *Suppose  $\Psi \in V_0(N)$  satisfies  $\underline{\mathbf{L}}^2\Psi = \mathcal{L}\Psi$  and  $\underline{\mathbf{S}}^2\Psi = \mathcal{S}\Psi$ . Then  $\underline{\mathbf{L}}^2(\ast\Psi) = \mathcal{L}(\ast\Psi)$  and  $\underline{\mathbf{S}}^2(\ast\Psi) = \mathcal{S}(\ast\Psi)$ . Furthermore, if  $L_3\Psi = M\Psi$ ,  $S_3\Psi = M_s\Psi$ , and  $\hat{R}\Psi = p\Psi$ , then  $L_3(\ast\Psi) = -M(\ast\Psi)$ ,  $S_3(\ast\Psi) = -M_s(\ast\Psi)$ , and  $\hat{R}(\ast\Psi) = p(\ast\Psi)$ .*

*Proof.* Direct calculations using the second quantized forms of  $\underline{\mathbf{L}}$  and  $\underline{\mathbf{S}}$  show that both operators anticommute with  $\ast$  on  $V_0(N)$ . The results for angular momentum and spin are then trivial. The result for the inversion operator follows from the fact that the parity of a wavefunction is equivalent to the parity of the number of  $p$ -orbitals present in each Slater determinant (since  $\hat{R}\varphi_{ns}\alpha = \varphi_{ns}\alpha$  for both  $n = 1$  and  $2$ , and  $\hat{R}\varphi_{2p_i}\alpha = -\varphi_{2p_i}\alpha$  for  $i = 1, 2, 3$ ) and the number of  $p$ -orbitals in the dual of a Slater determinant with  $k$   $p$ -orbitals is  $6 - k$ , preserving the parity.  $\square$

The above result is a modest generalization of insights by spectroscopists (who did not know they were speaking what mathematicians would call supersymmetry). They introduced the dual of a configuration with respect to a single open shell (termed “conjugate configuration” in [Con80]), and noticed that it gives rise to the same set of  $L_3$  and  $S_3$  eigenvalues [Con80] and, what is more, the same  $\underline{\mathbf{L}}^2$ ,  $\underline{\mathbf{S}}^2$ , and  $\underline{\mathbf{L}} \cdot \underline{\mathbf{S}}$  matrices [CS35].

**6.3. Simultaneous  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  eigenspaces.** We now form the joint angular momentum and spin eigenspaces within  $V_0(N)$ . Lemma 6.2 shows that we only need to do this for lithium-carbon; the remaining cases follow by duality. Under the restriction of a fixed number of  $1s$ ,  $2s$ ,  $2p$  orbitals, the results were no doubt known to early spectroscopists, who realized that the multiplet structure of observed spectra can only be captured via superposition of Aufbau principle Slater determinants into “terms” (in our language, joint  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  eigenspaces); see, e.g., [CS35, Con80]. We do not, however, know of a complete tabulation.

THEOREM 6.1. *For the lithium-neon sequences ( $N = 3, \dots, 10$ ,  $Z > 0$ ), orthonormal bases for the  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  simultaneous eigenspaces within  $V_0(N)$  are as given in Tables 4–11. See below for the notation used in the tables.*

*Proof.* We give only the proof for the highest dimensional case, carbon, the other cases being analogous but easier.

By Lemma 6.1, it suffices to find the joint  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  eigenstates in the four-electron vector space spanned by  $\mathcal{B} = \{|\psi_{i_1}\psi_{i_2}\psi_{i_3}\psi_{i_4}\rangle \mid 1 \leq i_1 < i_2 < i_3 < i_4 \leq 8\}$ , with the  $\psi_i$  as in (29).

We note first that each Slater determinant in the above basis is already an eigenfunction of  $\underline{\mathbf{S}}_3$ , and that the space with  $S_3$  eigenvalue  $M$  is isomorphic (by flipping all spins) to that with eigenvalue  $-M$ . Since both  $\underline{\mathbf{L}}^2$  and  $\underline{\mathbf{S}}^2$  commute with  $S_3$ , it suffices therefore to consider their action on the eigenspaces of  $S_3$  with eigenvalue  $M \geq 0$ .

Next we observe that within each such  $S_3$  eigenspace, the span of those Slater determinants which share the same number of different spatial orbitals (4, 3, or 2) is also invariant under  $\underline{\mathbf{L}}^2$  and  $\underline{\mathbf{S}}^2$ .

We now calculate the matrices of  $\underline{\mathbf{L}}^2$  and  $\underline{\mathbf{S}}^2$  with respect to the so-obtained subsets of the basis  $\mathcal{B}$ , using (32), (33), and the formulae from subsection 6.1. To shorten the notation, we will write  $s \uparrow$ ,  $s \downarrow$ ,  $p_i \uparrow$ ,  $p_i \downarrow$  instead of  $\varphi_{2s} \uparrow$ ,  $\varphi_{2s} \downarrow$ ,  $\varphi_{2p_i} \uparrow$ ,  $\varphi_{2p_i} \downarrow$ .

**Four different spatial orbitals,  $M = 2$ .** On  $|s \uparrow p_1 \uparrow p_2 \uparrow p_3 \uparrow\rangle$ ,

$$\underline{\mathbf{L}}^2 = 0, \quad \underline{\mathbf{S}}^2 = 6.$$

**Four different spatial orbitals,  $M = 1$ .** With respect to the basis  $\{|s \uparrow p_1 \uparrow p_2 \uparrow p_3 \downarrow\rangle, |s \uparrow p_1 \uparrow p_2 \downarrow p_3 \uparrow\rangle, |s \uparrow p_1 \downarrow p_2 \uparrow p_3 \uparrow\rangle, |s \downarrow p_1 \uparrow p_2 \uparrow p_3 \uparrow\rangle\}$ ,

$$\underline{\mathbf{L}}^2 = \begin{pmatrix} 4 & -2 & -2 & 0 \\ -2 & 4 & -2 & 0 \\ -2 & -2 & 4 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad \underline{\mathbf{S}}^2 = \begin{pmatrix} 3 & 1 & 1 & 1 \\ 1 & 3 & 1 & 1 \\ 1 & 1 & 3 & 1 \\ 1 & 1 & 1 & 3 \end{pmatrix}.$$

**Four different spatial orbitals,  $M = 0$ .** With respect to the basis  $\{|s \uparrow p_1 \uparrow p_2 \downarrow p_3 \downarrow\rangle, |s \uparrow p_1 \downarrow p_2 \uparrow p_3 \downarrow\rangle, |s \uparrow p_1 \downarrow p_2 \downarrow p_3 \uparrow\rangle, |s \downarrow p_1 \downarrow p_2 \uparrow p_3 \uparrow\rangle, |s \downarrow p_1 \uparrow p_2 \downarrow p_3 \uparrow\rangle, |s \downarrow p_1 \uparrow p_2 \uparrow p_3 \downarrow\rangle\}$ ,

$$\underline{\mathbf{L}}^2 = \begin{pmatrix} 4 & -2 & -2 & 0 & 0 & 0 \\ -2 & 4 & -2 & 0 & 0 & 0 \\ -2 & -2 & 4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4 & -2 & -2 \\ 0 & 0 & 0 & -2 & 4 & -2 \\ 0 & 0 & 0 & -2 & -2 & 4 \end{pmatrix}, \quad \underline{\mathbf{S}}^2 = \begin{pmatrix} 2 & 1 & 1 & 0 & 1 & 1 \\ 1 & 2 & 1 & 1 & 0 & 1 \\ 1 & 1 & 2 & 1 & 1 & 0 \\ 0 & 1 & 1 & 2 & 1 & 1 \\ 1 & 0 & 1 & 1 & 2 & 1 \\ 1 & 1 & 0 & 1 & 1 & 2 \end{pmatrix}.$$

**Three different spatial orbitals,  $M = 1$ .** On each Slater determinant  $|s \uparrow s \downarrow p_i \uparrow p_j \uparrow\rangle$ , and each Slater determinant  $|p_k \uparrow p_k \downarrow p_i \uparrow p_j \uparrow\rangle$ ,

$$\underline{\mathbf{L}}^2 = 2, \quad \underline{\mathbf{S}}^2 = 2.$$

(In total, these span a six-dimensional subspace.) With respect to each basis  $\{|p_i \uparrow p_i \downarrow s \uparrow p_j \uparrow\rangle, |p_k \uparrow p_k \downarrow s \uparrow p_j \uparrow\rangle\}$ ,

$$\underline{\mathbf{L}}^2 = \begin{pmatrix} 4 & -2 \\ -2 & 4 \end{pmatrix}, \quad \underline{\mathbf{S}}^2 = 2.$$

(In total, these span a six-dimensional subspace.)

**Three different spatial orbitals,  $M = 0$ .** With respect to each of the bases  $\{|s \uparrow s \downarrow p_i \uparrow p_j \downarrow\rangle, |s \uparrow s \downarrow p_i \downarrow p_j \uparrow\rangle\}$  and  $\{|p_k \uparrow p_k \downarrow p_i \uparrow p_j \downarrow\rangle, |p_k \uparrow p_k \downarrow p_i \downarrow p_j \uparrow\rangle\}$ ,

$$\underline{\mathbf{L}}^2 = \begin{pmatrix} 4 & -2 \\ -2 & 4 \end{pmatrix}, \quad \underline{\mathbf{S}}^2 = \begin{pmatrix} 4 & -2 \\ -2 & 4 \end{pmatrix}.$$

(In total, these span a 12-dimensional subspace.) With respect to each of the bases  $\{|p_i \uparrow p_i \downarrow s \uparrow p_j \downarrow\rangle, |p_k \uparrow p_k \downarrow s \uparrow p_j \downarrow\rangle, |p_i \uparrow p_i \downarrow s \downarrow p_j \uparrow\rangle, |p_k \uparrow p_k \downarrow s \downarrow p_j \uparrow\rangle\}$ ,

$$\underline{\mathbf{L}}^2 = \begin{pmatrix} 4 & -2 & 0 & 0 \\ -2 & 4 & 0 & 0 \\ 0 & 0 & 4 & -2 \\ 0 & 0 & -2 & 4 \end{pmatrix}, \quad \underline{\mathbf{S}}^2 = \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{pmatrix}.$$

(In total, these span a 12-dimensional subspace.)

**Two different spatial orbitals,  $M = 0$ .** With respect to the bases  $\{|s \uparrow s \downarrow p_1 \uparrow p_1 \downarrow\rangle, |s \uparrow s \downarrow p_2 \uparrow p_2 \downarrow\rangle, |s \uparrow s \downarrow p_3 \uparrow p_3 \downarrow\rangle\}$  and  $\{|p_1 \uparrow p_1 \downarrow p_2 \uparrow p_2 \downarrow\rangle, |p_2 \uparrow p_2 \downarrow p_3 \uparrow p_3 \downarrow\rangle, |p_3 \uparrow p_3 \downarrow p_1 \uparrow p_1 \downarrow\rangle\}$ ,

$$\underline{\mathbf{L}}^2 = \begin{pmatrix} 4 & -2 & -2 \\ -2 & 4 & -2 \\ -2 & -2 & 4 \end{pmatrix}, \quad \underline{\mathbf{S}}^2 = 0.$$

This completes the explicit description of the action of  $\underline{\mathbf{L}}^2$  and  $\underline{\mathbf{S}}^2$ .

The eigenfunctions and eigenvalues are now found by explicit diagonalization of the above matrices.  $\square$

Tables 4–11 use the following conventions:

- (1) The two 1s orbitals present in every Slater determinant are not shown.
- (2) The eigenfunctions are not normalized.
- (3) In all cases, it is assumed that  $i = 1, 2, 3$ ,  $(i, j) = (1, 2), (2, 3), (3, 1)$ , and  $(i, j, k)$  is any cyclic permutation of  $(1, 2, 3)$ . In particular, any eigenfunction containing a variable corresponds to a three-dimensional subspace.

(4) Eigenfunctions of the form  $a\Psi_1 + b\Psi_2 + c\Psi_3$  are such that  $a + b + c = 0$  and stand for two linearly independent orthogonal choices of  $(a, b, c)$ , and hence correspond to a two-dimensional subspace.

(5) Within each  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  eigenspace, the different  $S_3$  eigenspaces are separated by a line, in the order  $M = S, -S, S - 1, -(S - 1), \dots, 0$ .

(6) The spin orbitals  $\varphi_{2s} \uparrow, \varphi_{2s} \downarrow, \varphi_{2p_i} \uparrow, \varphi_{2p_i} \downarrow$  are abbreviated  $s, \bar{s}, p_i, \bar{p}_i$ .

Note that the parity of the eigenfunctions in the tables, although not shown explicitly, can be read off by counting the number of  $p$  orbitals (see the previous section).

TABLE 4  
Lithium sequence  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$   
eigenspaces.

	$\underline{\mathbf{S}}^2 = \frac{3}{4}$
$\underline{\mathbf{L}}^2 = 0$	$\frac{ s\rangle}{ \bar{s}\rangle}$
$\underline{\mathbf{L}}^2 = 2$	$\frac{ p_i\rangle}{ \bar{p}_i\rangle}$

TABLE 5  
Beryllium sequence  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  eigenspaces.

	$\underline{\mathbf{S}}^2 = 0$	$\underline{\mathbf{S}}^2 = 2$
$\underline{\mathbf{L}}^2 = 0$	$\frac{ s\bar{s}\rangle}{ p_1\bar{p}_1\rangle +  p_2\bar{p}_2\rangle +  p_3\bar{p}_3\rangle}$	
$\underline{\mathbf{L}}^2 = 2$	$\frac{ s\bar{p}_i\rangle -  \bar{s}p_i\rangle}{ s\bar{p}_i\rangle +  \bar{s}p_i\rangle}$	$\frac{ p_i p_j\rangle}{ \bar{p}_i \bar{p}_j\rangle}$
$\underline{\mathbf{L}}^2 = 6$	$\frac{ p_i \bar{p}_j\rangle -  \bar{p}_i p_j\rangle}{a p_1\bar{p}_1\rangle + b p_2\bar{p}_2\rangle + c p_3\bar{p}_3\rangle}$	$\frac{ p_i \bar{p}_j\rangle +  \bar{p}_i p_j\rangle}{ p_i \bar{p}_j\rangle +  \bar{p}_i p_j\rangle}$

TABLE 6  
 Boron sequence  $\underline{\mathbf{L}}^2\text{-}\underline{\mathbf{S}}^2$  eigenspaces.

	$\underline{\mathbf{S}}^2 = \frac{3}{4}$	$\underline{\mathbf{S}}^2 = \frac{15}{4}$
$\underline{\mathbf{L}}^2 = 0$	$\frac{ sp_1\bar{p}_1\rangle +  sp_2\bar{p}_2\rangle +  sp_3\bar{p}_3\rangle}{ \bar{s}p_1\bar{p}_1\rangle +  \bar{s}p_2\bar{p}_2\rangle +  \bar{s}p_3\bar{p}_3\rangle}$	$\frac{ p_1p_2p_3\rangle}{ \bar{p}_1\bar{p}_2\bar{p}_3\rangle}$ $\frac{ p_1p_2\bar{p}_3\rangle +  p_1\bar{p}_2p_3\rangle +  \bar{p}_1p_2p_3\rangle}{ \bar{p}_1p_2p_3\rangle +  \bar{p}_1p_2\bar{p}_3\rangle +  p_1p_2p_3\rangle}$
$\underline{\mathbf{L}}^2 = 2$	$\frac{\frac{ s\bar{s}p_i\rangle}{ p_i p_j \bar{p}_j\rangle +  p_i p_k \bar{p}_k\rangle} - 2 \bar{s}p_i p_j\rangle -  \bar{s}p_i p_k\rangle}{\frac{ s\bar{s}p_i\rangle}{ \bar{p}_i \bar{p}_j \bar{p}_j\rangle +  \bar{p}_i \bar{p}_k \bar{p}_k\rangle} - 2 \bar{s}p_i \bar{p}_j\rangle -  \bar{s}p_i \bar{p}_k\rangle}$	$\frac{ sp_i p_j\rangle}{ \bar{s}p_i \bar{p}_j\rangle}$ $\frac{ sp_i \bar{p}_j\rangle +  \bar{s}p_i p_j\rangle +  \bar{s}p_i p_k\rangle}{ \bar{s}p_i \bar{p}_j\rangle +  \bar{s}p_i \bar{p}_k\rangle +  \bar{s}p_i p_j\rangle}$
$\underline{\mathbf{L}}^2 = 6$	$\frac{\frac{ sp_i \bar{p}_j\rangle -  \bar{s}p_i p_j\rangle}{a sp_1\bar{p}_1\rangle + b sp_2\bar{p}_2\rangle + c sp_3\bar{p}_3\rangle} - \frac{ p_i p_j \bar{p}_j\rangle -  p_i p_k \bar{p}_k\rangle}{a \bar{p}_3 p_1 p_2\rangle + b \bar{p}_3 p_1 \bar{p}_2\rangle + c \bar{p}_3 \bar{p}_1 p_2\rangle}}{\frac{ s\bar{s}p_i\rangle}{a \bar{s}p_1\bar{p}_1\rangle + b \bar{s}p_2\bar{p}_2\rangle + c \bar{s}p_3\bar{p}_3\rangle} - \frac{ p_i p_j \bar{p}_j\rangle -  p_i p_k \bar{p}_k\rangle}{a \bar{p}_3 p_1 \bar{p}_2\rangle + b \bar{p}_3 \bar{p}_1 p_2\rangle + c \bar{p}_3 \bar{p}_1 p_2\rangle}}$	

Inspecting these eigenspaces reveals a number of interesting properties.

COROLLARY 6.1. *For any  $N = 3, \dots, 10$ , the maximum dimension of any simultaneous eigenspace within  $V_0(N)$  of the operators (7) is two.*

As regards diagonalization of the Hamiltonian, this is clearly much more promising than the 70-dimensional space of carbon.

COROLLARY 6.2. *For any  $N = 3, \dots, 10$  and any simultaneous  $\underline{\mathbf{L}}^2\text{-}\underline{\mathbf{S}}^2\text{-}L_3\text{-}S_3\text{-}\hat{R}$  eigenspace within  $V_0(N)$  with  $L_3$  eigenvalue equal to zero, all Slater determinants occurring within the space differ by an even number of orbitals.*

This is remarkable and will greatly simplify the structure of the Hamiltonian matrix in the basis (30), due to the simpler structure of Slater’s rules (see below). Also, it implies that even for the correlated eigenstates of the Hamiltonian, the orbitals (29) are natural orbitals in the sense of Löwdin. A more abstract proof of Corollary 6.2 will be given elsewhere.

**6.4. Symbolic interaction matrix.** In order to calculate the Hamiltonian matrix  $PHP$  on each  $\underline{\mathbf{L}}^2\text{-}\underline{\mathbf{S}}^2\text{-}\hat{R}$  eigenspace, note first that  $PHP$  commutes with (7) (see Lemma 4.1, which remains valid for the more general orbitals (31); cf. the calculus in section 6.1). Hence it suffices to pick arbitrary components of  $\underline{\mathbf{L}}$  and  $\underline{\mathbf{S}}$ , say  $L_3$  and  $S_3$ , and calculate this matrix on the  $\underline{\mathbf{L}}^2\text{-}L_3\text{-}\underline{\mathbf{S}}^2\text{-}S_3\text{-}\hat{R}$  eigenspace with maximal  $S_3$  and  $L_3 = 0$ . These spaces are shown in Tables 12–14. Here, because of their importance for the interaction energy, the  $1s$  orbitals are shown and the eigenfunctions are normalized. We find it convenient to abbreviate the spin orbitals

$$(35) \quad \varphi_{1s} \uparrow, \varphi_{1s} \downarrow, \varphi_{2s} \uparrow, \varphi_{2s} \downarrow, \varphi_{2p_3} \uparrow, \varphi_{2p_3} \downarrow, \varphi_{2p_1} \uparrow, \varphi_{2p_1} \downarrow, \varphi_{2p_2} \uparrow, \varphi_{2p_2} \downarrow$$

(even more drastically than in Tables 4–11) by

$$(36) \quad 1, \bar{1}, 2, \bar{2}, 3, \bar{3}, 4, \bar{4}, 5, \bar{5}.$$

Thus, for example, the top carbon state of Table 13,

$$\frac{1}{\sqrt{3}}(|1\bar{1}2\bar{2}3\bar{3}\rangle + |1\bar{1}2\bar{2}4\bar{4}\rangle + |1\bar{1}2\bar{2}5\bar{5}\rangle),$$



TABLE 8  
Nitrogen sequence  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  eigenspaces.

	$\underline{\mathbf{S}}^2 = \frac{3}{4}$	$\underline{\mathbf{S}}^2 = \frac{15}{4}$
$\underline{\mathbf{L}}^2 = 0$	$\frac{ sp_1\overline{p_1}p_2\overline{p_2}\rangle +  sp_1\overline{p_1}p_3\overline{p_3}\rangle +  sp_2\overline{p_2}p_3\overline{p_3}\rangle}{ \overline{sp_1}\overline{p_1}p_2\overline{p_2}\rangle +  \overline{sp_1}\overline{p_1}p_3\overline{p_3}\rangle +  \overline{sp_2}\overline{p_2}p_3\overline{p_3}\rangle}$	$\frac{ s\overline{sp_1}p_2p_3\rangle}{ s\overline{sp_1}p_2\overline{p_3}\rangle}$ $\frac{ s\overline{sp_1}\overline{p_2}p_3\rangle +  s\overline{sp_1}p_2p_3\rangle +  s\overline{sp_1}p_2\overline{p_3}\rangle}{ s\overline{sp_1}\overline{p_2}p_3\rangle +  s\overline{sp_1}p_2\overline{p_3}\rangle +  s\overline{sp_1}p_2p_3\rangle}$
$\underline{\mathbf{L}}^2 = 2$	$\frac{ s\overline{sp_i}p_j\overline{p_j}\rangle +  s\overline{sp_i}p_k\overline{p_k}\rangle}{ p_1p_2p_3\overline{p_j}\overline{p_k}\rangle}$ $\frac{2 \overline{sp_i}\overline{p_i}p_jp_k\rangle -  sp_i\overline{p_i}p_jp_k\rangle -  sp_i\overline{p_i}p_j\overline{p_k}\rangle}{ s\overline{sp_i}p_j\overline{p_j}\rangle +  s\overline{sp_i}p_k\overline{p_k}\rangle}$ $\frac{ p_1p_2p_3p_jp_k\rangle}{2 sp_i\overline{p_i}p_j\overline{p_k}\rangle -  \overline{sp_i}\overline{p_i}p_jp_k\rangle -  \overline{sp_i}\overline{p_i}p_j\overline{p_k}\rangle}$	$\frac{ sp_1p_2p_3\overline{p_i}\rangle}{ sp_1p_2p_3p_i\rangle}$ $\frac{ sp_i\overline{p_i}p_j\overline{p_k}\rangle +  sp_i\overline{p_i}p_jp_k\rangle +  \overline{sp_i}\overline{p_i}p_jp_k\rangle}{ sp_i\overline{p_i}p_jp_k\rangle +  \overline{sp_i}\overline{p_i}p_j\overline{p_k}\rangle +  \overline{sp_i}\overline{p_i}p_jp_k\rangle}$
$\underline{\mathbf{L}}^2 = 6$	$\frac{ s\overline{sp_i}p_j\overline{p_j}\rangle -  s\overline{sp_i}p_k\overline{p_k}\rangle}{a s\overline{sp_1}p_2\overline{p_3}\rangle + b s\overline{sp_1}p_2p_3\rangle + c s\overline{sp_1}p_2p_3\rangle}$ $\frac{ sp_i\overline{p_i}p_jp_k\rangle -  sp_i\overline{p_i}p_j\overline{p_k}\rangle}{a sp_1\overline{p_1}p_2\overline{p_2}\rangle + b sp_1\overline{p_1}p_3\overline{p_3}\rangle + c sp_2\overline{p_2}p_3\overline{p_3}\rangle}$ $\frac{ s\overline{sp_i}p_j\overline{p_j}\rangle -  s\overline{sp_i}p_k\overline{p_k}\rangle}{a s\overline{sp_1}p_2p_3\rangle + b s\overline{sp_1}p_2\overline{p_3}\rangle + c s\overline{sp_1}p_2\overline{p_3}\rangle}$ $\frac{ \overline{sp_i}\overline{p_i}p_jp_k\rangle -  \overline{sp_i}\overline{p_i}p_j\overline{p_k}\rangle}{a \overline{sp_1}\overline{p_1}p_2\overline{p_2}\rangle + b \overline{sp_1}\overline{p_1}p_3\overline{p_3}\rangle + c \overline{sp_2}\overline{p_2}p_3\overline{p_3}\rangle}$	

TABLE 9  
Oxygen sequence  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  eigenspaces.

	$\underline{\mathbf{S}}^2 = 0$	$\underline{\mathbf{S}}^2 = 2$
$\underline{\mathbf{L}}^2 = 0$	$\frac{ s\overline{sp_1}\overline{p_1}p_2\overline{p_2}\rangle +  s\overline{sp_1}\overline{p_1}p_3\overline{p_3}\rangle +  s\overline{sp_2}\overline{p_2}p_3\overline{p_3}\rangle}{ p_1\overline{p_1}p_2\overline{p_2}p_3\overline{p_3}\rangle}$	
$\underline{\mathbf{L}}^2 = 2$	$ \overline{sp_1}\overline{p_2}p_3p_jp_k\rangle -  \overline{sp_1}p_2p_3\overline{p_j}\overline{p_k}\rangle$	$\frac{ s\overline{sp_1}p_2p_3\overline{p_i}\rangle}{ sp_1p_2p_3\overline{p_j}\overline{p_k}\rangle}$ $\frac{ s\overline{sp_1}p_2p_3p_i\rangle}{ \overline{sp_1}p_2\overline{p_3}p_jp_k\rangle}$ $\frac{ s\overline{sp_i}\overline{p_i}p_j\overline{p_k}\rangle +  s\overline{sp_i}\overline{p_i}p_jp_k\rangle}{ sp_1p_2p_3p_jp_k\rangle +  \overline{sp_1}p_2p_3\overline{p_j}\overline{p_k}\rangle}$
$\underline{\mathbf{L}}^2 = 6$	$\frac{ s\overline{sp_i}\overline{p_i}p_j\overline{p_k}\rangle -  s\overline{sp_i}\overline{p_i}p_jp_j\rangle}{a s\overline{sp_1}\overline{p_1}p_2\overline{p_2}\rangle + b s\overline{sp_1}\overline{p_1}p_3\overline{p_3}\rangle + c s\overline{sp_2}\overline{p_2}p_3\overline{p_3}\rangle}$	

TABLE 10  
Fluorine sequence  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  eigenspaces.

	$\underline{\mathbf{S}}^2 = \frac{3}{4}$
$\underline{\mathbf{L}}^2 = 0$	$\frac{ sp_1\overline{p_1}p_2\overline{p_2}p_3\overline{p_3}\rangle}{ \overline{sp_1}\overline{p_1}p_2\overline{p_2}p_3\overline{p_3}\rangle}$
$\underline{\mathbf{L}}^2 = 2$	$\frac{ s\overline{sp_1}p_2p_3\overline{p_i}\overline{p_j}\rangle}{ s\overline{sp_1}p_2p_3p_ip_j\rangle}$

TABLE 11  
Neon sequence  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$  eigenspaces.

	$\underline{\mathbf{S}}^2 = 0$
$\underline{\mathbf{L}}^2 = 0$	$ s\overline{sp_1}\overline{p_1}p_2\overline{p_2}p_3\overline{p_3}\rangle$

stands for

$$\frac{1}{\sqrt{3}} \left( |\varphi_{1s}\uparrow \varphi_{1s}\downarrow \varphi_{2s}\uparrow \varphi_{2s}\downarrow \varphi_{2p_3}\uparrow \varphi_{2p_3}\downarrow\rangle + |\varphi_{1s}\uparrow \varphi_{1s}\downarrow \varphi_{2s}\uparrow \varphi_{2s}\downarrow \varphi_{2p_1}\uparrow \varphi_{2p_1}\downarrow\rangle \right. \\ \left. + |\varphi_{1s}\uparrow \varphi_{1s}\downarrow \varphi_{2s}\uparrow \varphi_{2s}\downarrow \varphi_{2p_2}\uparrow \varphi_{2p_2}\downarrow\rangle \right).$$

We begin by analyzing the  $V_{ee}$  matrix elements between the eigenfunctions of Tables 12–14. Using Slater’s rules [SO96, section 2.3], these are straightforward to express in terms of Coulomb and exchange integrals ( $aa|bb$ ) and ( $ab|ba$ ) of the spatial orbitals (31), where (in common notation)

$$(37) \quad (ab|cd) = \int_{\mathbb{R}^6} dx_1 dx_2 a^*(x_1) b(x_1) \frac{1}{|x_1 - x_2|} c^*(x_2) d(x_2).$$

LEMMA 6.3. *Let  $N \in \{3, \dots, 10\}$ . Orthonormal bases of the simultaneous  $\underline{\mathbf{L}}^2$ - $\underline{\mathbf{S}}^2$ - $L_3$ - $S_3$ - $\hat{R}$  eigenspaces within  $V_0(N)$  with  $S_3$  maximal and  $L_3 = 0$ , and the corresponding  $V_{ee}$  matrix elements  $\langle \Psi | V_{ee} | \tilde{\Psi} \rangle$  in terms of Coulomb and exchange integrals of the one-electron orbitals (31), are as given in Tables 12–14. Here the orbitals are abbreviated as in (35)–(36), and the off-diagonal matrix elements ( $\Psi \neq \tilde{\Psi}$ ) in the two-dimensional eigenspaces are denoted by “cross.”*

The shortness of the expressions for the  $\langle \Psi | V_{ee} | \tilde{\Psi} \rangle$ , and the absence of Coulomb and exchange integrals involving the last orbital, comes from the absence of single excitations (Corollary 6.2) and the equivalence of the  $p$  orbitals in (31) up to rotation. The latter would be destroyed by changing to a basis of  $L_3$  eigenfunctions (which is why we have not done so even though this would have been more convenient for the diagonalization of  $\underline{\mathbf{L}}^2$  in the previous subsection).

**6.5. Explicit interaction matrix.** In order to obtain explicit values, we finally need to substitute the explicit PT orbitals (24), (25) and evaluate the ensuing Coulomb and exchange integrals. We do this via a four-step procedure: reduce the original integrals over  $\mathbb{R}^6$  to integrals over  $\mathbb{R}^3$  via Fourier transform calculus; explicitly determine the Fourier transforms of pointwise products of the above orbitals; reduce to one-dimensional integrals with the help of spherical polar coordinates in Fourier space; evaluate the remaining one-dimensional integrals, which turn out to have rational integrands.

The Fourier transform of a function  $f \in L^1(\mathbb{R}^n)$  will be denoted  $\hat{f}$ ; we find it convenient to use the definition

$$(38) \quad \hat{f}(k) := \int_{\mathbb{R}^n} f(x) e^{-ik \cdot x} dx,$$

which does not contain any normalization constants.

LEMMA 6.4. *For one-electron orbitals  $\psi_\alpha \in L^2(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$ , with  $\hat{\psi}_\alpha \in L^2(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$  and  $\alpha \in \{i, j, k, \ell\}$ , let  $f(x) := \psi_i(x) \psi_j^*(x)$  and  $g(x) := \psi_k^*(x) \psi_\ell(x)$ . Then*

$$(39) \quad (\psi_i \psi_j | \psi_k \psi_\ell) = \int_{\mathbb{R}^6} dx_1 dx_2 \psi_i^*(x_1) \psi_j(x_1) \frac{1}{|x_1 - x_2|} \psi_k^*(x_2) \psi_\ell(x_2) \\ = \frac{1}{2\pi^2} \int_{\mathbb{R}^3} dk \frac{1}{|k|^2} (\hat{f})^*(k) \hat{g}(k).$$

Note that this shows that exchange integrals ( $\psi_i \psi_j | \psi_j \psi_i$ ) are positive.

TABLE 12

$V_{ee}$  matrix element expressions for the Li-B sequences; “cross” denotes the off-diagonal term in the  $2 \times 2$  matrix. See Lemma 6.3 for notation.

	$\underline{L}^2$	$\underline{S}^2$	$\hat{R}$	$\Psi$	$\langle V_{ee} \rangle$
Li	0	$\frac{3}{4}$	1	$ 1\bar{1}2\rangle$	$(11 11) + 2(11 22) - (12 21)$
	2	$\frac{3}{4}$	-1	$ 1\bar{1}3\rangle$	$(11 11) + 2(11 33) - (13 31)$
Be	0	0	1	$ 1\bar{1}2\bar{2}\rangle$	$(11 11) + 4(11 22) - 2(12 21) + (22 22)$
				$\frac{1}{\sqrt{3}}( 1\bar{1}3\bar{3}\rangle +  1\bar{1}4\bar{4}\rangle +  1\bar{1}5\bar{5}\rangle)$	$(11 11) + 4(11 33) - 2(13 31) + (33 33) + 2(34 43)$
				cross	$\sqrt{3}(23 32)$
	2	0	-1	$\frac{1}{\sqrt{2}}( 1\bar{1}2\bar{3}\rangle -  1\bar{1}2\bar{3}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 2(11 33) - (13 31) + (22 33) + (23 32)$
				$ 1\bar{1}23\rangle$	$(11 11) + 2(11 22) - (12 21) + 2(11 33) - (13 31) + (22 33) - (23 32)$
	2	2	-1	$ 1\bar{1}23\rangle$	$(11 11) + 2(11 22) - (12 21) + 2(11 33) - (13 31) + (22 33) - (23 32)$
$ 1\bar{1}45\rangle$				$(11 11) + 4(11 33) - 2(13 31) + (33 44) - (34 43)$	
6	0	1	$\frac{1}{\sqrt{6}}(2 1\bar{1}3\bar{3}\rangle -  1\bar{1}4\bar{4}\rangle -  1\bar{1}5\bar{5}\rangle)$	$(11 11) + 4(11 33) - 2(13 31) + (33 33) - (34 43)$	
B	0	$\frac{3}{4}$	1	$\frac{1}{\sqrt{3}}( 1\bar{1}23\bar{3}\rangle +  1\bar{1}24\bar{4}\rangle +  1\bar{1}25\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 4(11 33) - 2(13 31) + 2(22 33) - (23 32) + (33 33) + 2(34 43)$
	0	$\frac{15}{4}$	-1	$ 1\bar{1}345\rangle$	$(11 11) + 6(11 33) - 3(13 31) + 3(33 44) - 3(34 43)$
	2	$\frac{3}{4}$	-1	$ 1\bar{1}2\bar{2}3\rangle$	$(11 11) + 4(11 22) - 2(12 21) + 2(11 33) - (13 31) + (22 22) + 2(22 33) - (23 32)$
				$\frac{1}{\sqrt{2}}( 1\bar{1}34\bar{4}\rangle +  1\bar{1}35\bar{5}\rangle)$	$(11 11) + 6(11 33) - 3(13 31) + (33 33) + 2(33 44)$
				cross	$\sqrt{2}(23 32)$
	2	$\frac{15}{4}$	1	$\frac{1}{\sqrt{6}}(2 1\bar{1}245\rangle -  1\bar{1}24\bar{5}\rangle -  1\bar{1}24\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 4(11 33) - 2(13 31) + 2(22 33) + (23 32) + (33 44) - (34 43)$
				$ 1\bar{1}245\rangle$	$(11 11) + 2(11 22) - (12 21) + 4(11 33) - 2(13 31) + 2(22 33) - 2(23 32) + (33 44) - (34 43)$
	6	$\frac{3}{4}$	1	$\frac{1}{\sqrt{6}}(2 1\bar{1}23\bar{3}\rangle -  1\bar{1}24\bar{4}\rangle -  1\bar{1}25\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 4(11 33) - 2(13 31) + 2(22 33) - (23 32) + (33 33) - (34 43)$
				-1	$\frac{1}{\sqrt{6}}(2 1\bar{1}345\rangle -  1\bar{1}34\bar{5}\rangle -  1\bar{1}34\bar{5}\rangle)$

*Proof.* Since the  $\psi_\alpha$  are in  $L^2(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$ , their products  $f$  and  $g$  are in  $L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$  and hence their Fourier transforms are well defined. Consider the integral  $I(\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} dx dy \frac{e^{-\lambda|x-y|}}{|x-y|} f^*(x)g(y)$ ,  $\lambda > 0$ . It is easy to show that  $\frac{e^{-\lambda|x|}}{|x|} = \frac{4\pi}{\lambda^2 + |k|^2}$ . Since  $f, g \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$  it follows that  $|\frac{e^{-\lambda|x-y|}}{|x-y|} f^*(x)g(y)| \in L^1(\mathbb{R}^6)$  and so by dominated convergence

$$(40) \quad I(\lambda) \rightarrow \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} dx dy \frac{1}{|x-y|} f^*(x)g(y) \quad (\lambda \rightarrow 0).$$

Setting  $h = e^{-\lambda|x|}/|x|$  we have  $I(\lambda) = \int_{\mathbb{R}^3} dy (f * h)(y)g(y)dy$  and  $\widehat{f * h} = \hat{f} \hat{h} \in L^1(\mathbb{R}^3)$  since  $\hat{f} \in L^1(\mathbb{R}^3)$  and  $\hat{h} \in L^\infty(\mathbb{R}^3)$ . By Plancherel’s theorem we have  $I(\lambda) = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} dk \frac{4\pi}{\lambda^2 + |k|^2} (\hat{f})^*(k) \hat{g}(k)$ , and again by dominated convergence and using  $f, g \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$ ,

$$(41) \quad I(\lambda) \rightarrow \frac{1}{2\pi^2} \int_{\mathbb{R}^3} dk \frac{1}{|k|^2} (\hat{f})^*(k) \hat{g}(k) \quad (\lambda \rightarrow 0).$$



TABLE 13

$V_{ee}$  matrix element expressions for the C sequence; “cross” denotes the off-diagonal term in the  $2 \times 2$  matrix. See Lemma 6.3 for notation.

	$\underline{L}^2$	$\underline{S}^2$	$\hat{R}$	$\Psi$	$\langle V_{ee} \rangle$
C	0	0	1	$\frac{1}{\sqrt{3}}( 1\bar{1}2\bar{2}3\bar{3}\rangle +  1\bar{1}2\bar{2}4\bar{4}\rangle +  1\bar{1}2\bar{2}5\bar{5}\rangle)$	$(11 11) + 4(11 22) - 2(12 21) + 4(11 33) - 2(13 31) + (22 22) + 4(22 33) - 2(23 32) + (33 33) + 2(34 43)$
				$\frac{1}{\sqrt{3}}( 1\bar{1}3\bar{3}4\bar{4}\rangle +  1\bar{1}3\bar{3}5\bar{5}\rangle +  1\bar{1}4\bar{4}5\bar{5}\rangle)$	$(11 11) + 8(11 33) - 4(13 31) + 2(33 33) + 4(33 44)$
				cross	$2(23 32)$
	0	2	-1	$\frac{1}{\sqrt{12}}(3 1\bar{1}2\bar{3}4\bar{5}\rangle -  1\bar{1}2\bar{3}4\bar{5}\rangle -  1\bar{1}2\bar{3}4\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 6(11 33) - 3(13 31) + 3(22 33) + (23 32) + 3(33 44) - 3(34 43)$
				$ 1\bar{1}2\bar{3}4\bar{5}\rangle$	$(11 11) + 2(11 22) - (12 21) + 6(11 33) - 3(13 31) + 3(22 33) - 3(23 32) + 3(33 44) - 3(34 43)$
	2	0	-1	$\frac{1}{2}( 1\bar{1}2\bar{3}4\bar{4}\rangle -  1\bar{1}2\bar{3}4\bar{4}\rangle +  1\bar{1}2\bar{3}5\bar{5}\rangle -  1\bar{1}2\bar{3}5\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 6(11 33) - 3(13 31) + 3(22 33) + (33 33) + 2(33 44)$
				cross	$(23 32)$
	2	2	1	$ 1\bar{1}2\bar{2}4\bar{5}\rangle$	$(11 11) + 4(11 22) - 2(12 21) + 4(11 33) - 2(13 31) + (22 22) + 4(22 33) - 2(23 32) + (33 44) - (34 43)$
				$ 1\bar{1}3\bar{3}4\bar{5}\rangle$	$(11 11) + 8(11 33) - 4(13 31) + (33 33) + 5(33 44) - 3(34 43)$
				cross	$(23 32)$
	2	2	-1	$\frac{1}{\sqrt{2}}( 1\bar{1}2\bar{3}4\bar{4}\rangle +  1\bar{1}2\bar{3}5\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 6(11 33) - 3(13 31) + 3(22 33) - 2(23 32) + (33 33) + 2(33 44)$
				cross	$(23 32)$
				cross	$(23 32)$
	6	0	1	$\frac{1}{\sqrt{6}}(2 1\bar{1}2\bar{2}3\bar{3}\rangle -  1\bar{1}2\bar{2}4\bar{4}\rangle -  1\bar{1}2\bar{2}5\bar{5}\rangle)$	$(11 11) + 4(11 22) - 2(12 21) + 4(11 33) - 2(13 31) + (22 22) + 4(22 33) - 2(23 32) + (33 33) - (34 43)$
				$\frac{1}{\sqrt{6}}(2 1\bar{1}4\bar{4}5\bar{5}\rangle -  1\bar{1}3\bar{3}4\bar{4}\rangle -  1\bar{1}3\bar{3}5\bar{5}\rangle)$	$(11 11) + 8(11 33) - 4(13 31) + 2(33 33) + 4(33 44) - 3(34 43)$
cross				$-(23 32)$	
-1			$\frac{1}{\sqrt{12}}(2 1\bar{1}2\bar{3}4\bar{5}\rangle -  1\bar{1}2\bar{3}4\bar{5}\rangle -  1\bar{1}2\bar{3}4\bar{5}\rangle + 2 1\bar{1}2\bar{3}4\bar{5}\rangle -  1\bar{1}2\bar{3}4\bar{5}\rangle -  1\bar{1}2\bar{3}4\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 6(11 33) - 3(13 31) + 3(22 33) + 3(33 44)$	
6	2	-1	$\frac{1}{\sqrt{6}}(2 1\bar{1}2\bar{3}4\bar{5}\rangle -  1\bar{1}2\bar{3}4\bar{5}\rangle -  1\bar{1}2\bar{3}4\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 6(11 33) - 3(13 31) + 3(22 33) - 2(23 32) + 3(33 44)$	
			cross	$-(23 32)$	

Combining (40) and (41) gives the result.  $\square$

Next we calculate the Fourier transforms of pointwise products of the hydrogen orbitals (24), (25). Here and below, by expressions such as  $|x|e^{-\lambda|x|}(k)$  we mean the Fourier transform  $\hat{f}(k)$  of the function  $f(x) = |x|e^{-\lambda|x|}$ .

LEMMA 6.5. *With the Fourier transform as defined in (38), and  $\lambda > 0$ , we have the following table:*

Function	Fourier transform
$e^{-\lambda x }$	$\frac{8\lambda\pi}{(\lambda^2 +  k ^2)^2}$
$ x e^{-\lambda x }$	$\frac{32\lambda^2\pi}{(\lambda^2 +  k ^2)^3} - \frac{8\pi}{(\lambda^2 +  k ^2)^2}$
$ x ^2e^{-\lambda x }$	$\frac{192\lambda^3\pi}{(\lambda^2 +  k ^2)^4} - \frac{96\lambda\pi}{(\lambda^2 +  k ^2)^3}$
$x_j e^{-\lambda x }$	$-\frac{32i\lambda\pi k_j}{(\lambda^2 +  k ^2)^3}$
$x_j^2 e^{-\lambda x }$	$\frac{32\lambda\pi}{(\lambda^2 +  k ^2)^3} - \frac{192\lambda\pi k_j^2}{(\lambda^2 +  k ^2)^4}$
$x_\ell x_j e^{-\lambda x } (j \neq \ell)$	$-\frac{192\lambda\pi k_j k_\ell}{(\lambda^2 +  k ^2)^4}$
$ x x_j e^{-\lambda x }$	$\frac{32i\pi k_j}{(\lambda^2 +  k ^2)^3} - \frac{192i\lambda^2\pi k_j}{(\lambda^2 +  k ^2)^4}$

TABLE 14

$V_{ee}$  matrix element expressions for the  $N$ - $Ne$  sequences; “cross” denotes the off-diagonal term in the  $2 \times 2$  matrix. See Lemma 6.3 for notation.

	$\underline{L}^2$	$\underline{S}^2$	$\hat{R}$	$\Psi$	$\langle V_{ee} \rangle$
N	0	$\frac{3}{4}$	1	$\frac{1}{\sqrt{3}}( 1\bar{1}23\bar{3}4\bar{4}\rangle +  1\bar{1}23\bar{3}5\bar{5}\rangle +  1\bar{1}24\bar{4}5\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 8(11 33) - 4(13 31) + 4(22 33) - 2(23 32) + 2(33 33) + 4(33 44)$
	0	$\frac{15}{4}$	-1	$ 1\bar{1}2\bar{2}345\rangle$	$(11 11) + 4(11 22) - 2(12 21) + 6(11 33) - 3(13 31) + (22 22) + 6(22 33) - 3(23 32) + 3(33 44) - 3(34 43)$
	2	$\frac{3}{4}$	-1	$ 1\bar{1}34\bar{4}5\bar{5}\rangle$	$(11 11) + 10(11 33) - 5(13 31) + 2(33 33) + 8(33 44) - 4(34 43)$
				$\frac{1}{\sqrt{2}}( 1\bar{1}2\bar{2}34\bar{4}\rangle +  1\bar{1}2\bar{2}35\bar{5}\rangle)$	$(11 11) + 4(11 22) - 2(12 21) + 6(11 33) - 3(13 31) + (22 22) + 6(22 33) - 3(23 32) + (33 33) + 2(33 44)$
				cross	$\sqrt{2}(23 32)$
	1	$\frac{1}{\sqrt{6}}(2 1\bar{1}23\bar{3}4\bar{4}\rangle -  1\bar{1}23\bar{3}4\bar{4}\rangle -  1\bar{1}23\bar{3}4\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 8(11 33) - 4(13 31) + 4(22 33) + (33 33) + 5(33 44) - 3(34 43)$		
	2	$\frac{15}{4}$	1	$ 1\bar{1}2\bar{3}345\rangle$	$(11 11) + 2(11 22) - (12 21) + 8(11 33) - 4(13 31) + 4(22 33) - 3(23 32) + (33 33) + 5(33 44) - 3(34 43)$
	6	$\frac{3}{4}$	-1	$\frac{1}{\sqrt{6}}(2 1\bar{1}2\bar{2}34\bar{4}\rangle -  1\bar{1}2\bar{2}34\bar{4}\rangle -  1\bar{1}2\bar{2}34\bar{5}\rangle)$	$(11 11) + 4(11 22) - 2(12 21) + 6(11 33) - 3(13 31) + (22 22) + 6(22 33) - 3(23 32) + 3(33 44)$
				$\frac{1}{\sqrt{6}}(2 1\bar{1}24\bar{4}5\bar{5}\rangle -  1\bar{1}23\bar{3}4\bar{4}\rangle -  1\bar{1}23\bar{3}5\bar{5}\rangle)$	$(11 11) + 2(11 22) - (12 21) + 8(11 33) - 4(13 31) + 4(22 33) - 2(23 32) + 2(33 33) + 4(33 44) - 3(34 43)$
	O	0	0	1	$\frac{1}{\sqrt{3}}( 1\bar{1}23\bar{3}4\bar{4}\rangle +  1\bar{1}23\bar{3}5\bar{5}\rangle +  1\bar{1}24\bar{4}5\bar{5}\rangle)$
				$ 1\bar{1}334455\rangle$	$(11 11) + 12(11 33) - 6(13 31) + 3(33 33) + 12(33 44) - 6(34 43)$
				cross	$\sqrt{3}(23 32)$
2		0	-1	$\frac{1}{\sqrt{2}}( 1\bar{1}234455\rangle -  1\bar{1}234455\rangle)$	$(11 11) + 2(11 22) - (12 21) + 10(11 33) - 5(13 31) + 5(22 33) - (23 32) + 2(33 33) + 8(33 44) - 4(34 43)$
2		2	-1	$ 1\bar{1}234455\rangle$	$(11 11) + 2(11 22) - (12 21) + 10(11 33) - 5(13 31) + 5(22 33) - 3(23 32) + 2(33 33) + 8(33 44) - 4(34 43)$
				1	$ 1\bar{1}2\bar{2}3345\rangle$
6		0	1	$\frac{1}{\sqrt{6}}(2 1\bar{1}2\bar{2}4455\rangle -  1\bar{1}2\bar{2}3344\rangle -  1\bar{1}2\bar{2}3355\rangle)$	$(11 11) + 4(11 22) - 2(12 21) + 8(11 33) - 4(13 31) + (22 22) + 8(22 33) - 4(23 32) + 2(33 33) + 4(33 44) - 3(34 43)$
F	0	$\frac{3}{4}$	1	$ 1\bar{1}2334455\rangle$	$(11 11) + 2(11 22) - (12 21) + 12(11 33) - 6(13 31) + 6(22 33) - 3(23 32) + 3(33 33) + 12(33 44) - 6(34 43)$
	2	$\frac{3}{4}$	-1	$ 1\bar{1}2\bar{2}34455\rangle$	$(11 11) + 4(11 22) - 2(12 21) + 10(11 33) - 5(13 31) + (22 22) + 10(22 33) - 5(23 32) + 2(33 33) + 8(33 44) - 4(34 43)$
Ne	0	0	1	$ 1\bar{1}2\bar{2}334455\rangle$	$(11 11) + 4(11 22) - 2(12 21) + 12(11 33) - 6(13 31) + (22 22) + 12(22 33) - 6(23 32) + 3(33 33) + 12(33 44) - 6(34 43)$

*Proof.* Let  $f(x) := e^{-\lambda|x|}$ . We have  $\widehat{f}(k) = 8\pi\lambda/(\lambda^2 + |k|^2)^2$ , which is easy to verify by direct calculation (convert to spherical polar coordinates and integrate). All remaining Fourier transforms can be expressed in terms of derivatives of  $\widehat{f}$ , as follows. Using  $|x|e^{-\lambda|x|} = -\frac{d}{d\lambda}e^{-\lambda|x|}$ ,  $|x|^2e^{-\lambda|x|} = \frac{d^2}{d\lambda^2}e^{-\lambda|x|}$ , and noting that differentiation with respect to  $\lambda$  commutes with the Fourier transform gives

$$|\cdot|\widehat{e^{-\lambda|\cdot|}}(k) = -\frac{\partial}{\partial\lambda}\widehat{f}(k), \quad |\cdot|^2\widehat{e^{-\lambda|\cdot|}}(k) = \frac{d^2}{d\lambda^2}\widehat{f}(k).$$

For the next three Fourier transforms, we recall the well-known differentiation identities for Fourier transforms:

$$\widehat{x_j f}(k) = i\frac{\partial}{\partial k_j}\widehat{f}(k) \quad \text{and} \quad \widehat{x_\ell x_j f}(k) = -\frac{\partial^2}{\partial k_\ell \partial k_j}\widehat{f}(k).$$

Consequently

$$(\widehat{x_j e^{-\lambda|x|}})(k) = i\frac{\partial}{\partial k_j}\widehat{f}(k) \quad \text{and} \quad \widehat{x_j x_\ell e^{-\lambda|x|}}(k) = -\frac{\partial^2}{\partial k_j \partial k_\ell}\widehat{f}(k).$$

The final case needed is

$$(|x|\widehat{x_j e^{-\lambda|x|}})(k) = -\frac{d}{d\lambda}\left(i\frac{\partial}{\partial k_j}\widehat{f}(k)\right).$$

Working out the above derivatives of  $\widehat{f}$  explicitly is straightforward, yielding the formulae given in the lemma.  $\square$

LEMMA 6.6. *The Fourier transforms of pointwise products of the hydrogen orbitals (24), (25) are as given in the following table. In all cases  $j, \ell = 1, 2, 3, j \neq \ell$ .*

Function	Fourier transform
$\phi_{1s}\phi_{1s}$	$\frac{16Z^4}{(4Z^2+ k ^2)^2}$
$\phi_{2s}\phi_{2s}$	$\frac{2Z^4}{(Z^2+ k ^2)^2} - \frac{7Z^6}{(Z^2+ k ^2)^3} + \frac{6Z^8}{(Z^2+ k ^2)^4}$
$\phi_{1s}\phi_{2s}$	$\frac{4\sqrt{2}Z^4}{((\frac{3}{2}Z)^2+ k ^2)^2} - \frac{9\sqrt{2}Z^6}{((\frac{3}{2}Z)^2+ k ^2)^3}$
$\phi_{2p_j}\phi_{2p_j}$	$\frac{Z^6}{(Z^2+ k ^2)^3} - \frac{6Z^6 k_j^2}{(Z^2+ k ^2)^4}$
$\phi_{1s}\phi_{2p_j}$	$\frac{6\sqrt{2}iZ^5 k_j}{((\frac{3}{2}Z)^2+ k ^2)^3}$
$\phi_{2s}\phi_{2p_j}$	$\frac{6Z^7 i k_j}{(Z^2+ k ^2)^4} - \frac{3Z^5 i k_j}{(Z^2+ k ^2)^3}$
$\phi_{2p_j}\phi_{2p_\ell}$	$-\frac{6k_j k_\ell Z^6}{(Z^2+ k ^2)^4}$

*Proof.* This is simply an application of the results of Lemma 6.5.  $\square$

Finally we use these Fourier transforms, along with the reformulation of the Coulomb and exchange integrals from Lemma 6.4, to derive the explicit values of these integrals.

LEMMA 6.7. *Using the abbreviated notation  $1 = \phi_{1s}, 2 = \phi_{2s}, 3 = \phi_{2p_3}, 4 = \phi_{2p_1}, 5 = \phi_{2p_2}$ , the Coulomb and exchange integrals (37) occurring in Tables 12–14 with the PT orbitals (24), (25) are given by the following table:*

(11 11)	(11 22)	(12 21)	(22 22)	(11 33)	(13 31)	(22 33)	(23 32)	(33 33)	(33 44)	(34 43)
$\frac{5}{8}Z$	$\frac{17}{81}Z$	$\frac{16}{729}Z$	$\frac{77}{512}Z$	$\frac{59}{243}Z$	$\frac{112}{6561}Z$	$\frac{83}{512}Z$	$\frac{15}{512}Z$	$\frac{501}{2560}Z$	$\frac{447}{2560}Z$	$\frac{27}{2560}Z$

*Proof.* We insert the Fourier transforms from Lemma 6.6 into (39), change to spherical polar coordinates, and integrate. The angular integrals are elementary and the final radial integrals, which on account of Lemmas 6.6 and 6.4 have rational integrands, may be evaluated with Maple; for a truly pen and paper method, one can use complex contour integration.  $\square$

Note the interesting multiscale effect that the exchange integrals are much smaller than the Coulomb integrals, by about one order of magnitude. Nevertheless, as we will see later, the exchange terms play an important role in energy level splitting.

The table in the above lemma, together with Tables 12–14, completes the task of evaluating the matrix  $PV_{ee}P$  on  $V_0(N)$ .

**6.6. The matrix  $PHP$ .** The remaining part  $PH_0P$  of the Hamiltonian  $PHP$  is trivial to determine, because the space  $V_0(N)$  is an eigenspace of  $H_0$ , with eigenvalue given in Lemma 5.1:

$$(42) \quad H_0 = PH_0P = Z^2 \left( -1 - \frac{N-2}{8} \right) I \text{ on } V_0(N).$$

By inspection of (42), Lemma 6.7, and Tables 12–14 we obtain an interesting corollary.

**COROLLARY 6.3.** *The matrix of the PT Hamiltonian  $PHP$  with respect to the basis in Tables 12–14 with the orbitals (24), (25) is a rational matrix.*

**7. Atomic energy levels and eigenstates.** The spectral decomposition of the PT Hamiltonians  $PHP$  is almost immediate from the block form derived in the previous section, the only remaining task being the diagonalization of the  $2 \times 2$  blocks, which may be done explicitly: For (orthonormal) wavefunctions  $\Psi_1$ ,  $\Psi_2$  and  $E_i := \langle \Psi_i | H | \Psi_i \rangle$ , the eigenvalues are given by

$$(43) \quad \lambda_{\pm} = \frac{E_1 + E_2}{2} \pm \sqrt{\left( \frac{E_1 - E_2}{2} \right)^2 + |\langle \Psi_1 | V_{ee} | \Psi_2 \rangle|^2}$$

with corresponding normalized eigenstates

$$(44) \quad \Psi_{\pm} = \frac{1}{\sqrt{1 + c_{\pm}^2}} \left( \Psi_1 + c_{\pm} \Psi_2 \right), \quad c_{\pm} = \frac{\frac{E_2 - E_1}{2} \pm \sqrt{\left( \frac{E_1 - E_2}{2} \right)^2 + |\langle \Psi_1 | V_{ee} | \Psi_2 \rangle|^2}}{\langle \Psi_1 | V_{ee} | \Psi_2 \rangle}.$$

These formulae, together with (42), Tables 12–14, and Lemma 6.7, immediately yield the following theorem.

**THEOREM 7.1.** *For  $N = 3, \dots, 10$  and  $Z > 0$ , the energy levels of the PT model (16), (17) are as given in Tables 15 and 16. Each eigenspace has the minimal dimension  $(2L + 1)(2S + 1)$  possible for its spin and angular momentum quantum numbers  $L$  and  $S$  (see Lemma 2.1), and the up-to-normalization unique corresponding eigenstate with zero  $L_3$  and maximal  $S_3$  is as shown in the tables. Moreover the levels and eigenstates in the tables provide the leading order asymptotic terms of the true Schrödinger levels as  $Z \rightarrow \infty$ , in the sense described in Theorem 4.1.*

Note that the ordering of the PT levels is independent of  $Z$ , since the spectral gaps are linear in  $Z$ .

**8. Comparison with experiment and methods in the physics and chemistry literature.** The analytical eigenvalues and eigenstates derived in the isoelectronic limit provide a wealth of information on various quantities of physical and

TABLE 15

Asymptotic Schrödinger energy levels and eigenstates (= exact PT levels and states) for the Li-C sequences. The numerical values are for  $Z=N$ .  $\Psi$  is the up-to-normalization unique PT eigenstate with  $L_3 = 0$  and maximal  $S_3$ . The  $\Psi_i$  are as in Tables 12–13, labeled by order of appearance, with  $1, 2, 3, 4, 5, \bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{5}$  as in Theorem 3.1.

	Symm.	$\Psi$	$E$	$c$	$E$ (num.)	$c$ (num.)
Li	$2S$	$\Psi_1$	$\frac{5965}{8}Z^2 + \frac{5852}{8}Z$		-7.0566	
	$2P^o$	$\Psi_2$	$\frac{9}{8}Z^2 + \frac{57397}{8}Z$		-6.8444	
Be	$1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$\frac{1}{1679616}(2813231 - 5\sqrt{1509308377})Z$	$-\frac{1}{59049}(2\sqrt{1509308377} - 6981)\sqrt{3}$	-13.7629	-0.2311
	$3P^o$	$\Psi_4$	$\frac{1}{4}Z^2 + \frac{1363969}{839808}Z$		-13.5034	
	$1P^o$	$\Psi_3$	$\frac{5}{4}Z^2 + \frac{2826353}{1679616}Z$		-13.2690	
	$3P$	$\Psi_5$	$\frac{1}{2}Z^2 + \frac{839808}{1679616}Z$		-13.0955	
	$1D$	$\Psi_6$	$\frac{5}{4}Z^2 + \frac{14673197}{8398080}Z$		-13.0112	
	$1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$\frac{1}{1679616}(2813231 + 5\sqrt{1509308377})Z$		-12.8377	4.3271
B	$2P^o$	$\frac{1}{\sqrt{1+c^2}}(\Psi_3 + c\Psi_4)$	$-\frac{11}{8}Z^2 + \frac{6718464}{6718464}(16493659 - \sqrt{733174301809})Z$	$-\frac{1}{393660}(\sqrt{733174301809} - 809747)\sqrt{2}$	-22.7374	-0.1671
	$4P$	$\Psi_6$	$-\frac{11}{8}Z^2 + \frac{2906780}{40981549}Z$		-22.4273	
	$2D$	$\Psi_7$	$-\frac{11}{8}Z^2 + \frac{16796160}{4151299}Z$		-22.1753	
	$2S$	$\Psi_1$	$\frac{8}{8}Z^2 + \frac{1679616}{8322281}Z$		-22.0171	
	$2P$	$\Psi_5$	$-\frac{11}{8}Z^2 + \frac{2769436}{14301407}Z$		-21.9878	
	$4S^o$	$\Psi_8$	$-\frac{11}{8}Z^2 + \frac{2769436}{14301407}Z$		-21.7612	
	$2D^o$	$\Psi_2$	$-\frac{11}{8}Z^2 + \frac{5598720}{6718464}(16493659 + \sqrt{733174301809})Z$		-21.6030	5.9851
	$2P^o$	$\frac{1}{\sqrt{1+c^2}}(\Psi_3 + c\Psi_4)$	$-\frac{11}{8}Z^2 + \frac{6718464}{6718464}(16493659 - \sqrt{733174301809})Z$		-21.4629	
	$3P$	$\frac{1}{\sqrt{1+c^2}}(\Psi_6 + c\Psi_7)$	$-\frac{3}{2}Z^2 + \frac{3806107}{1119744} - \frac{1}{3359232}\sqrt{221876564389})Z$		-34.4468	-0.1056
	$1D$	$\frac{1}{\sqrt{1+c^2}}(\Psi_9 + c\Psi_{10})$	$-\frac{3}{2}Z^2 + \frac{19148633}{5598720} - \frac{1}{3359232}\sqrt{221876564389})Z$		-34.3202	0.1056
	$5S^o$	$\Psi_4$	$-\frac{3}{2}Z^2 + \frac{464555}{1399080}Z$		-34.0859	
	$1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{3}{2}Z^2 + \frac{1399080}{279936} - \frac{1}{1679616}\sqrt{62733275266})Z$		-34.1838	-0.2047
C	$3D^o$	$\Psi_{12}$	$-\frac{3}{2}Z^2 + \frac{4730843}{1399080}Z$		-33.7203	
	$3P^o$	$\Psi_8$	$-\frac{3}{2}Z^2 + \frac{150114}{559872}Z$		-33.5938	
	$1D^o$	$\Psi_{11}$	$-\frac{3}{2}Z^2 + \frac{9625711}{2799360}Z$		-33.3688	
	$3S^o$	$\Psi_3$	$-\frac{3}{2}Z^2 + \frac{961915}{279936}Z$		-33.3828	
	$1P^o$	$\Psi_5$	$-\frac{3}{2}Z^2 + \frac{68860}{1119744} - \frac{1}{3359232}\sqrt{221876564389})Z$		-33.2422	
	$3P$	$\frac{1}{\sqrt{1+c^2}}(\Psi_6 + c\Psi_7)$	$-\frac{3}{2}Z^2 + \frac{3806107}{1119744} + \frac{1}{3359232}\sqrt{221876564389})Z$		-32.7641	9.4668
	$1D$	$\frac{1}{\sqrt{1+c^2}}(\Psi_9 + c\Psi_{10})$	$-\frac{3}{2}Z^2 + \frac{19148633}{5598720} + \frac{1}{3359232}\sqrt{221876564389})Z$		-32.6376	-9.4668
	$1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{3}{2}Z^2 + \frac{966289}{279936} + \frac{1}{1679616}\sqrt{62733275266})Z$		-32.3943	4.8853

TABLE 16

Asymptotic Schrödinger energy levels and eigenstates (= exact PT levels and states) for the  $N$ -Ne sequences. The numerical values are for  $Z = N$ .  $\Psi$  is the up-to-normalization unique PT eigenstate with  $L_3 = 0$  and maximal  $S_3$ . The  $\Psi_i$  are as in Table 14, labeled by order of appearance, with  $1, 2, 3, 4, 5, \bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{5}$  as in Theorem 3.1.

	Symm.	$\Psi$	$E$	$c$	$E$ (num.)	$c$ (num.)			
N	$4S^o$	$\Psi_2$	$-\frac{13}{8}Z^2 + \frac{2437421}{559872}Z$	$-\frac{1}{393660}(\sqrt{1144203315841} - 1032821)\sqrt{2}$	-49.1503	-0.1324			
	$2D^o$	$\Psi_7$	$-\frac{13}{8}Z^2 + \frac{24551357}{5938720}Z$		-48.9288				
	$2P^o$	$\frac{1}{\sqrt{1+c^2}}(\Psi_4 + c\Psi_3)$	$-\frac{13}{8}Z^2 + \frac{6718461}{30636167 - \sqrt{1144203315841}}Z$		-48.8195				
	$4P$	$\Psi_6$	$-\frac{13}{8}Z^2 + \frac{7549145}{16337819}Z$		-48.1630				
	$2D$	$\Psi_8$	$-\frac{13}{8}Z^2 + \frac{76337819}{16796160}Z$		-47.8103				
	$2S$	$\Psi_1$	$-\frac{13}{8}Z^2 + \frac{3843463}{859808}Z$		-47.5888				
	$2P$	$\Psi_5$	$-\frac{13}{8}Z^2 + \frac{15395535}{3519232}Z$		-47.5478				
	$2P^o$	$\frac{1}{\sqrt{1+c^2}}(\Psi_4 + c\Psi_3)$	$-\frac{13}{8}Z^2 + \frac{6718461}{30636167 + \sqrt{1144203315841}}Z$		-46.5905		7.5532		
	O	$3P$	$\Psi_5$		$-\frac{7}{4}Z^2 + \frac{4754911}{839808}Z$		$-\frac{1}{295245}(2\sqrt{89111336179} - 572179)\sqrt{3}$	-66.7048	-0.1458
		$1D$	$\Psi_6$		$-\frac{7}{4}Z^2 + \frac{47729257}{8398080}Z$			-66.5360	
$1S$		$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{7}{4}Z^2 + \frac{1}{1679616}(9884485 - \sqrt{89111336179})Z$	-66.3421					
$3P^o$		$\Psi_4$	$-\frac{7}{4}Z^2 + \frac{1224899}{209952}Z$	-65.3265					
$1P^o$		$\Psi_3$	$-\frac{7}{4}Z^2 + \frac{9897607}{1679616}Z$	-64.8578					
$1S$		$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{7}{4}Z^2 + \frac{1}{1679616}(9884485 + \sqrt{89111336179})Z$	-63.4984	6.8592				
F		$2P^o$	$\Psi_2$	$-\frac{15}{8}Z^2 + \frac{11982943}{4082617}Z$		-87.6660			
	$2S$	$\Psi_1$	$-\frac{15}{8}Z^2 + \frac{4108267}{559872}Z$	-85.8342					
	$1S$	$\Psi_1$	$-2Z^2 + \frac{2455271}{279836}Z$	-112.2917					
Ne	$1S$	$\Psi_1$							

chemical interest, and yield a number of insights into the inner working mechanisms of the many-electron Schrödinger equation which are not readily available from numerical simulations.

We will discuss, in turn, the obtained  $L$  and  $S$  values, ground state dimensions, ground state energies, and spectral orderings.

### 8.1. $L$ and $S$ values and the notion of “group” in the periodic table.

The ground states themselves are not accessible from experiment, but their spin and angular momentum quantum numbers are. As already mentioned, the theoretical values agree with the experimental values in every case (see Table 3), not just for large  $Z$  but all the way down to neutral atoms ( $Z = N$ ), capturing the nontrivial dependence on the number of electrons.

An important theoretical feature of  $L$  and  $S$  values as compared to the more familiar semiempirical concept of “hydrogen orbital configurations” is that regardless of the approximations made to predict them in practice, they remain well defined in the full Schrödinger equation. See section 2. It would therefore be of value to base quantum mechanical explanations of the periodic table on numbers such as these. In this context we note that  $L$  and  $S$  values suffice to explain quantum mechanically a large part of the notion of “group” in the periodic table. Only five different  $(L, S)$  pairs occur mathematically for the first 10 atoms, and experimentally for the first 20. Now these correspond precisely to group 1 (alkali metals), the union of groups 2 and 8 (alkaline earth metals and noble gases), the union of groups 3 and 7 (group 3 metals and halogens), the union of groups 4 and 6 (carbon group and oxygen group), and group 5 (nitrogen group). See the table below.

<b>H</b>							<b>He</b>
<b>Li</b>	<b>Be</b>	<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	<b>Ne</b>
<b>Na</b>	<b>Mg</b>	<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	<b>Ar</b>
$L=0$ $S=1/2$	$L=0$ $S=0$	$L=1$ $S=1/2$	$L=1$ $S=1$	$L=0$ $S=3/2$			

Moreover, taking into account the gradients of  $L$  or  $S$  with respect to atomic number  $N$  would separate the group 3 metals from the halogens, and the carbon group from the oxygen group. Note that  $L$  and  $S$  gradients are mathematically analogous to ionization energies, which are gradients of energy with respect to  $N$ .

**8.2. Ground state dimensions.** These dimensions are shown in Table 3. They are interesting since they are a measure of the “flexibility” within the ground state, in that they specify the number of degrees of freedom which can be varied without affecting the energy of the state. This flexibility appears to be curiously unexplored in the literature, perhaps in part due to it not being clearly captured by the semiempirical Bohr–Slater picture, the Hartree–Fock approximation, or Kohn–Sham density functional theory.

On a qualitative level, we expect that an atom with a high-dimensional ground state will form a wider range of molecules than an atom with a similar number of valence electrons but with a lower-dimensional ground state. This should be true both in terms of molecular geometry (e.g., linear, bent, triangular, tetrahedral) as well as in terms of which atoms it will stably bond with. We plan to develop this idea in a more mathematical way in a future publication.

**8.3. Ground state energies.** The asymptotic ground state energies, despite being theoretically justified only for strongly positive ions (see section 4), still capture around 90% of the experimental [RJK<sup>+</sup>07] energies of neutral atoms. See the following table.

Atom	Li	Be	B	C	N	O	F	Ne
$E_{PT}$	-7.0566	-13.7629	-22.7374	-34.4468	-49.1503	-66.7048	-87.6660	-112.2917
$E_{exp}$	-7.4779	-14.6684	-24.6581	-37.8558	-54.6117	-75.1080	-99.8060	-129.0500
Error	5.6%	6.2%	7.8%	9.0%	10.0%	11.2%	12.2%	13.0%

**8.4. Spectral orderings and Hund's rule.** The spectral orderings of the asymptotic levels are in spectacular agreement with the experimental data [Huh93, RJK<sup>+</sup>07], even for neutral atoms. For the purpose of these comparisons we consider only the experimental states attributed to configurations containing only orbitals with  $n \leq 2$ . The results differ only by the interchange of two higher levels in beryllium ( $^1D$  and  $^3P$ ) and carbon ( $^1D^o$  and  $^3S^o$ ).

A key virtue of our exact eigenstates is that they allow us to trace the spectral gaps to the size of individual Coulomb and exchange integrals.

As an example of a  $2s$ - $2p$  spectral gap, consider the  $^2S$  ground state and  $^2P$  first excited state of lithium. Table 13 shows that the gap is given by the difference in interaction of the  $2p$  and  $2s$  orbitals with the  $1s$  shell,  $[2(11|33) - (13|31)] - [2(11|22) - (12|21)]$ .

As an example of energy level splitting between two states with an equal number of  $1s$ ,  $2s$ , and  $2p$  orbitals, consider the  $^4S^o$  ground state and  $^2D^o$  first excited state of nitrogen. A look at Table 14 reveals that the energy difference consists only of the exchange term  $-3(34|43)$ , which is present in the ground state due to the parallel spins of the three  $p$ -orbitals, but absent in the excited state.

In a large majority of cases, the theoretical orderings also agree with Hund's rules. In fact, many of Hund's rules are rigorous theorems in first order perturbation theory and related models, and they rely only on the structure of the symbolic matrices in Tables 12–14, not their numerical values. This will be discussed elsewhere.

Let us also describe a counterexample.

*Counterexample to Hund's rules.* Consider the higher carbon  $1s^2 2s 2p^3$  states. Hund's rules would order their energies, regardless of the choice of nuclear charge  $Z$ , as

$$E_{5S^o} < E_{3D^o} < E_{3P^o} < E_{3S^o} < E_{1D^o} < E_{1P^o}.$$

For large  $Z$  this agrees with the PT and experimental orderings. (That the latter two agree with each other follows from Theorem 4.1.)

But experimentally, at  $Z = 20$  the  $^1D^o$  singlet and the  $^3S^o$  triplet are observed to cross; see [RJK<sup>+</sup>07] and Figure 1. (This crossing is beautifully confirmed by theoretical calculations based on a simple configuration-interaction model designed with the help of our asymptotic findings here; see [FG09].) In particular, in the neutral atom,  $Z = N$ , the experimental ordering is

$$E_{5S^o} < E_{3D^o} < E_{3P^o} < E_{1D^o} < E_{3S^o} < E_{1P^o}.$$

This is an important example because it shows that it is of value to investigate which of Hund's rules can be justified quantum mechanically and which ones cannot. In this particular case, a closer look shows that there should be no universal ordering, neither



one way nor the other. The energy difference as read off from Table 13 consists of a  $2s-2p$  positive exchange term and a  $2p-2p$  negative exchange term

$$(45) \quad E_{3S^o} - E_{1D^o} = (24|42) - 3(34|43),$$

and so could have either sign, depending on the orbitals.

Note that this interesting effect is missed when the states under investigation are modeled by their Aufbau principle configurations. By Hund's rules, these are  $|1\bar{1}234\bar{5}\rangle$  for the singlet and  $|1\bar{1}234\bar{5}\rangle$  for the triplet. A simple calculation shows that the energy difference is then  $E_{3S^o} - E_{1D^o} = -(24|42) < 0$ , which is very far from the correct difference (45) and incorrectly predicts a universal ordering.

**8.5. Spectral gaps.** The asymptotic energy levels, despite their excellent orderings, do not give quantitatively useful spectral gaps for neutral atoms. However, in the regime of highly positive ions in which they were theoretically justified (see Theorem 4.1) they beautifully match the experimental gaps, as shown in Figure 1.

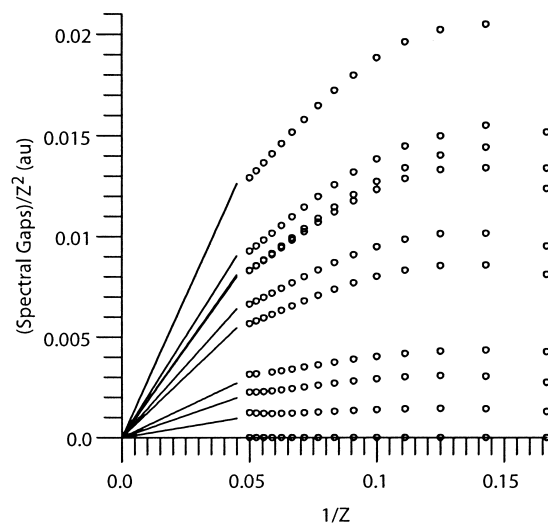


FIG. 1. *Splitting of noninteracting carbon ground state energy by electron interaction. Lines: asymptotic Schrödinger levels (this paper); circles: experimental data [RJK<sup>+</sup>07, Moo70]. For the highest level at  $Z = 6$  and the fourth level at  $Z = 18$ , we were unable to find experimental data.*

For the carbon series ( $N = 6$ ,  $Z = 6, 7, 8, \dots$ ), we show the experimental spectral gaps

$$\frac{E_j(N, Z)}{Z^2} - \frac{E_1(N, Z)}{Z^2}$$

(circles) and the perturbation-theoretic spectral gaps

$$\frac{E_j^{PT}(N, Z)}{Z^2} - \frac{E_1^{PT}(N, Z)}{Z^2} = \frac{\tilde{E}_j^{(1)}}{Z} - \frac{\tilde{E}_1^{(1)}}{Z}$$

(lines) against  $\frac{1}{Z}$ , with the energy of the lowest level (which shifts with  $Z$ ) having been subtracted for clarity. By Theorem 4.1, the match between PT and Schrödinger energy levels would become even better as  $Z$  increases further. But beyond the value

$Z = 20$  shown here, the match between Schrödinger levels and experiment slowly starts to deviate, due to the onset of relativistic effects, whose study lies beyond the scope of the present paper.

**8.6. Overall conclusion.** The principal conclusion of this paper is that the semiempirical hydrogen orbital configurations of atoms developed by Bohr, Hund, and Slater have a precise mathematical meaning, as asymptotic limits of the true Schrödinger ground states for large nuclear charge. (This holds up to certain small but interesting corrections, as described in section 3.1.) We hope that the limit eigenstates calculated here (see Table 2) can serve as a theoretical alternative to semiempirical discussions of the periodic table in the literature.

Another use of our findings, as benchmark data for the design and validation of computational methods, is explored in a companion paper [FG09].

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