Konrad-Zuse-Zentrum für Informationstechnik Berlin

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Abstract. Using the perturbational–variational Rayleigh–Ritz matrix formalism, the 1/Z–expansion for the ground state of the isoelectronic H_2 sequence in the range of the internuclear distance $0.2 \leq R \leq 9.0$ is calculated. Also lower bounds of the radius of convergence, based on Kato's theory of linear operators, are given. The numerical results of the 1/Z–expansion can be compared with the exact results and do not converge in the whole R–range. This behavior is in qualitative agreement with the lower bounds for the radius of convergence and enlights some still open properties of 1/Z–expansions for this sequence in the literature.

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Contents

1. Introduction

In [1] we described how the members of a sequence of isoelectronic diatomic molecules can be treated simultaneously in a numerically efficient way. But from the theoretical point of view it would be preferable to get electronic energies and wave functions of all molecules of an isoelectronic sequence as common functions of the continuous parameter Z. This would reflect (and perhaps give new insights into) the similar structure of the problems due to their relationship under the 1/Z–transformation. This was first suggested for atoms in 1930 by E. Hylleraas [12], who treated the isoelectronic Helium atom sequence. Such expansions of the electronic ground state energy of the He–atom, as well as studies of their radius of convergence and analytical behavior have reached up to now a sophisticated level. An excellent review can be found in [3]. Less good efforts, as we shall later substantiate, can be seen for the 1/Z–expansions for diatomic molecules. First of all such treatments for molecules are more cumbersome and inaccurate, and secondly problems are also introduced by the methods used and evidently by the finite radius of convergence. We focus this work on the 1/Z–expansion of the ground state energy of H_2. For this molecule a number of 1/Z–expansions and very accurate results can be found in the literature.

To get the 1/Z–expansion the Hylleraas–Knight–Sherr (HKS) method [12, 17] most commonly has been used. By a HKS–expansion to third order, B. Kirtmann *et al.* [15] got the energy -1.888104 for H_2 at R= 1.4. This is surprising because the difference of this value to the exact result of W. Kolos *et al.* [18, 19, 20] is only 0.66 mH(artree). Later work of R.L. Matcha *et al.* [21], B. Kirtman *et al.* [16] and J. Goodisman [9] extend this result to higher precision. But although Matcha *et al.* used the most accurate basis, they got in third order an energy which lies above the corresponding energies of the other mentioned works. See therefore Table 1.1. Matcha *et al.* also showed that the expansion coeffients $\tilde{\epsilon}_n$ for even n do not decrease uniformly by enlarging their James–Coolidge basis. This is in contradiction to the variational principle [12] on which the HKS–method is based. Even the odd order expansion of the energy can swing below the exact energy (see for example [16]), despite the fact that the exact Rayleigh–Schrödinger (RS) perturbation expansion of the energy to odd order must give upper bounds to the exact energy [26, 23].

The explanation for this behavior is well–known: The variational principle for $\tilde{\epsilon}_{2n}$ and $\tilde{\phi}_n$ involves the knowledge of the *exact* $\phi_0, \phi_1, \ldots, \phi_{n-1}$ and $\epsilon_0, \epsilon_1, \ldots, \epsilon_{2n-1}$. This may play a minor role for the expansion of atomic sequences, where very accurate treatments are possible, but for molecular systems, especially if the exact results are not known a priori, this is a crucial point.

Table 1.1: 1/Z–expansion for the H_2 at $R = 1.4$

	Ref. [15]	Ref. [16]	Ref. [9]	Ref. [21]	PVRR[a]
$\tilde{\epsilon}_0$	-2.568489	-2.568538	-2.56854	-2.568538	-2.568520
$\tilde{\epsilon}_1$	0.780874	0.780883	0.78099	0.780883	0.780827
$\tilde{\epsilon}_2$	-0.110260	-0.11023	-0.1108	-0.110968	-0.108939
$\tilde{\epsilon}_3$	0.009771	0.00975	0.0108	0.009771	0.009003
S_3	-1.888104	-1.88813	-1.88854	-1.88769	-1.887629
$\tilde{\epsilon}_4$				-0.00094	-0.000199
$\tilde{\epsilon}_5$				-0.00011	-0.000251
S_5				-1.88872	-1.88808
$\tilde{\epsilon}_6$				-0.000066	0.000013
$\tilde{\epsilon}_7$				0.000092	-0.000001
S_7				-1.888694	-1.888067
S_{99}					-1.888071

[a] this calculation
$S_N = \sum_{n=0}^{N} \tilde{\epsilon}_n$
Exact values: $\epsilon_0 = -2.568538$, $\epsilon_1 = 0.780883$, electronic energy = -1.888760

To avoid such problems it is possible to compute the RS–expansion in a fixed (and truncated) basis space. This corresponds to a perturbation expansion of the exact solution projected in this finite basis space. Because the variational principle is also valid in a finite space, a perturbation expansion of this form lead to odd order energy sums, which again are upper bounds to the exact energy as well as upper bounds to the Rayleigh–Ritz upper bounds [10]. This can be done especially for high order expansions by using the perturbational–variational Rayleigh–Ritz (PVRR) method [24, 25]. More details are given in Section 2. Instead of James–Coolidge functions, like Matcha *et al.*, we use large gaussian basis sets. For the H_2 molecule this is not the best choice, but in this way the method can be applied without modifications to arbitrary molecules.[1]

[1] We have done similar work for the ground states of He_2^+, HeH^+ and HeH. These results will not be presented here.

By expansion to high orders (up to 99th order in the finite basis space) we can also study the influence of higher orders and can compare the results with the energies derived from direct diagonalisation of the parameter depending matrix families, i.e. the Rayleigh–Ritz upper bounds (see [1]). The remaining problems occur due to the finite convergence radius. We will discuss this in detail in Section 3.

2. The 1/Z–Expansion

We treat the Schrödinger equation for the electronic motion (without inclusion of the internuclear repulsion) for a homonuclear diatomic molecule with two electrons and nuclear charge Z

$$\hat{\mathrm{H}}_{el}\Psi(\vec{r}_1,\vec{r}_2,s_1,s_2,R) = \epsilon(R)\Psi(\vec{r}_1,\vec{r}_2,s_1,s_2,R). \tag{2.1}$$

The Hamiltonian $\hat{\mathrm{H}}_{el}$ is given by

$$\hat{\mathrm{H}}_{el} = -\sum_{i=1}^{2}\left(\frac{\Delta_i}{2} + \sum_{k=1}^{2}\frac{Z}{|\vec{R}_k - \vec{r}_i|}\right) + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\,. \tag{2.2}$$

We now apply the scaling transformation

$$\vec{r}\,'_i = \mu\vec{r}_i \text{ (electrons)}; \qquad \vec{R}'_K = \mu\vec{R}_K \text{ (nuclei)} \tag{2.3}$$

with the resulting relations

$$R' = \mu R \tag{2.4}$$

$$\epsilon_{el}(R) = \mu^2\,\epsilon'_{el}(R') \tag{2.5}$$

$$\psi(\vec{r}_i,s_i;R) = \mu^3\,\psi'(\vec{r}\,'_i,s_i;R')\,. \tag{2.6}$$

If the operator $\hat{\mathrm{H}}'_{el}$ is split into its one– and two–electron-parts, we obtain:

$$\hat{\mathrm{H}}'_{el} = \hat{\mathrm{H}}'_0 + 1/\mu\,\hat{\mathrm{H}}'_1 \tag{2.7}$$

with

$$\hat{\mathrm{H}}'_0 = \sum_{i=1}^{2}\hat{\mathrm{h}}'(i); \tag{2.8}$$

$$\hat{\mathrm{h}}'(i) = -\frac{\Delta'}{2} - \frac{Z}{\mu|\vec{R}'_a - \vec{r}\,'_i|} - \frac{Z}{\mu|\vec{R}'_b - \vec{r}\,'_i|} \tag{2.9}$$

$$\hat{\mathrm{H}}'_1 = \frac{1}{|\vec{r}\,'_1 - \vec{r}\,'_2|}\,. \tag{2.10}$$

By choosing $\mu = Z$ we take H_2 as our reference molecule and starting point for the perturbation expansion. $\hat{\mathrm{H}}'_0$ and $\hat{\mathrm{H}}'_1$ are now independent of μ, Z and we get the parameter–dependent Schrödinger equation

$$(\hat{\mathrm{H}}'_0 + 1/Z\,\hat{\mathrm{H}}'_1)\,\psi' = \epsilon'_{el}(Z)\,\psi' \tag{2.11}$$

for fixed values of R'. The parameter independent operators $\hat{\mathrm{H}}'_0$ and $\hat{\mathrm{H}}'_1$ can be approximated in a Rayleigh–Ritz basis of orthogonal Slater–determinants by large non–diagonal matrices H_0 and H_1. We choose the Multireference

Single and Double Excitations Configuration Interaction program by Buenker and Peyerimhoff (MRD-CI) [5, 6, 7, 8] and have to modify it in order to split the final CI–matrix $\mathbf{H}$, respectively, into its one– and two–electron parts $\mathbf{H}_0$ and $\mathbf{H}_1$. We apply the program to the reference molecule at a sufficient number of internuclear distances R' and obtain (for each value of R') a special matrix eigenvalue problem

$$(\mathbf{H}_0 + 1/Z\ \mathbf{H}_1)\ \vec{C} = \tilde{\epsilon}'(Z)\ \vec{C} \quad \text{with} \quad \tilde{\epsilon}'(Z) \geq \epsilon'_{el}(Z)\ . \tag{2.12}$$

To solve the parameter-dependent matrix eigenvalue problem (2.12), we are able to make use of the perturbation-variation-Rayleigh-Ritz procedure (PVRR) developed by Silverman *et al* [24, 25]. This expansion gives the energy as a function of the parameter $1/Z$ in high order.

3. Radius of Convergence

Here we want to get a lower bound for the convergence radius of the perturbation expansion in $1/Z$. Therefore the theory of linear operators (see for example [14]) as well as some well-known properties of the molecular Schrödinger operator will be used. We consider the operator

$$\hat{\mathrm{H}}(\kappa) = \hat{\mathrm{H}}_0 + \kappa\hat{\mathrm{H}}_I = -\sum_{i=1}^{2}\left(\frac{\Delta_i}{2} + \sum_{k=1}^{2}\frac{1}{\mid \vec{R}_k - \vec{r}_i \mid}\right) + \kappa\frac{1}{\mid \vec{r}_1 - \vec{r}_2 \mid} \tag{3.1}$$

for fixed $\vec{R}_1$, $\vec{R}_2$ and $\kappa = 1/Z$. The basis space is $L^2(\mathcal{R}^6)$ where $\hat{\mathrm{H}}(\kappa)$ is a self-adjoint operator. $\hat{\mathrm{H}}(\kappa)$ is also bound from below for any real κ. To give a lower bound for the convergence radius ρ we look for lower bounds of

$$\hat{\mathrm{H}}_0 - \beta\hat{\mathrm{H}}_I = -\sum_{i=1}^{2}\left(\frac{\alpha\Delta_i}{2} + \sum_{k=1}^{2}\frac{1}{\mid \vec{R}_k - \vec{r}_i \mid}\right) - \left((1-\alpha)\frac{\Delta_1 + \Delta_2}{2} + \frac{\beta}{\mid \vec{r}_1 - \vec{r}_2 \mid}\right) \tag{3.2}$$

with $0 < \alpha < 1$ and $0 \leq \beta$. The eigenvalues of the second part in (3.2) are restricted from below by $-\beta^2/(4(1-\alpha))$ [14, chapter VII, eq. 4.66] and the first term by the united atom limit $-4/\alpha$. This leads to

$$((\hat{\mathrm{H}}_0 - \beta\hat{\mathrm{H}}_I)u, u) \geq -\left(\frac{\beta^2}{4(1-\alpha)} + \frac{4}{\alpha}\right)(u, u) \quad . \tag{3.3}$$

Thus $\hat{\mathrm{H}}_I$ is bounded with respect to $\hat{\mathrm{H}}_0$, and $\hat{\mathrm{H}}(\kappa)$ forms an operator family of type (B_0) as well as of type (A) in the sense of Kato [14]. Inequality (3.3) can be written in the form

$$(\hat{\mathrm{H}}_I u, u) \leq b(\hat{\mathrm{H}}_0 u, u) + a(u, u) \tag{3.4}$$

with

$$a = \frac{1}{\beta}\left(\frac{\beta^2}{4(1-\alpha)} + \frac{4}{\alpha}\right) \quad , \quad b = \frac{1}{\beta} \quad . \tag{3.5}$$

A lower bound for the convergence radius is given by [13, eq. 5.5]

$$\rho_{lb} = \left\{ \inf_{\substack{\xi\in\Gamma \\ \mu\in\Sigma(\hat{\mathrm{H}}_0)}} \left|\frac{a + b\mu}{\mu - \xi}\right| \right\}^{-1} \tag{3.6}$$

where $\Sigma(\hat{\mathrm{H}}_0)$ is the spectrum of $\hat{\mathrm{H}}_0$ and Γ a curve (in the complex plane) enclosing only the eigenvalue of $\hat{\mathrm{H}}_0$ we are interested in. The spectrum of $\hat{\mathrm{H}}_0$ ($\Sigma(\hat{\mathrm{H}}_0)$) is well-known. The basis space of $L^2(\mathcal{R}^6)$ of $\hat{\mathrm{H}}_0$ can be regarded to

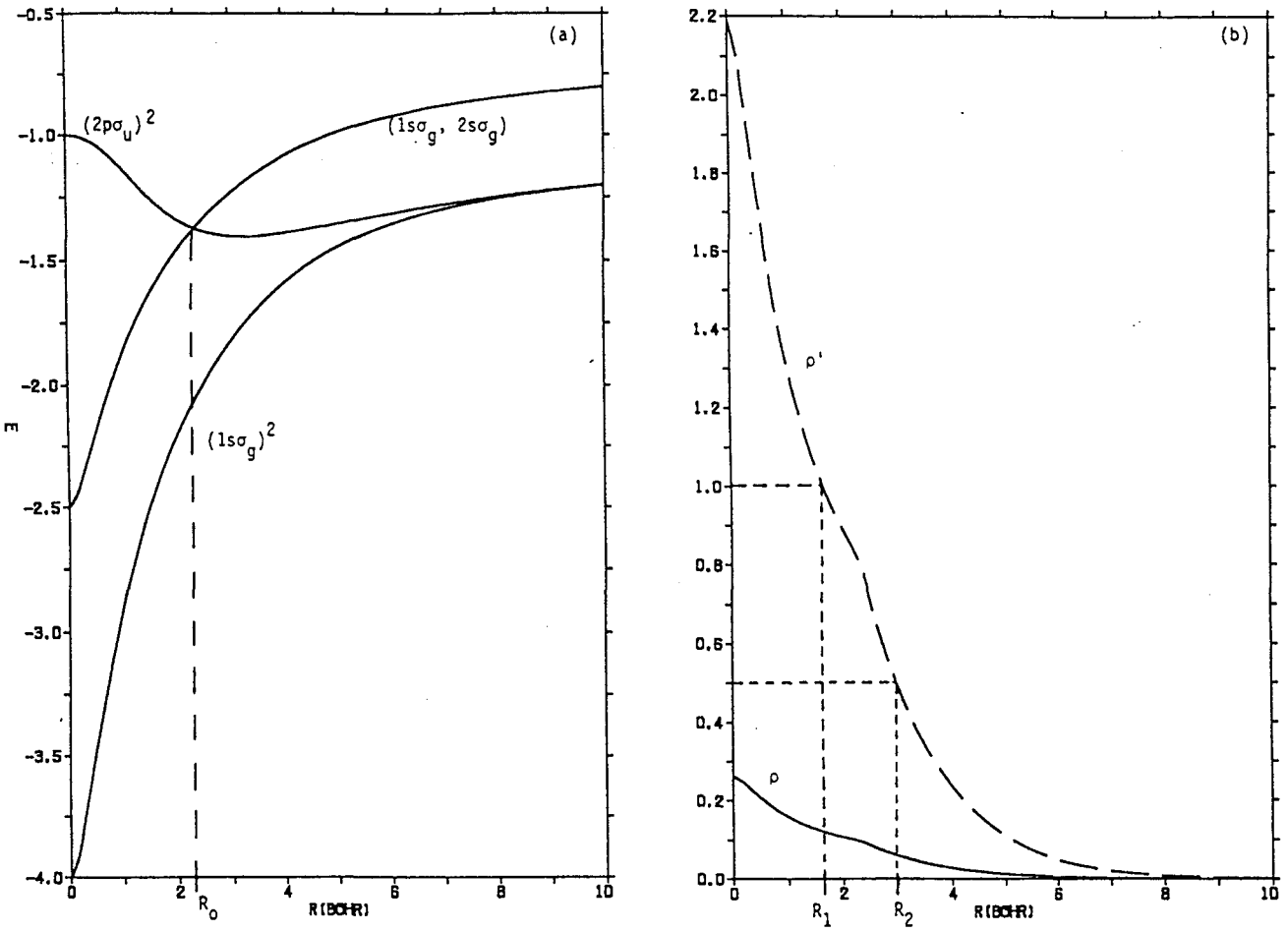

Figure 3.1: [a]The spectrum of the undisturbed operator ($R_0 \approx 2.3$). [b]The convergence radius ($R_1 \approx 1.7$ and $R_2 \approx 2.9$).

be the tensor product $L^2(\mathcal{R}^3) \otimes L^2(\mathcal{R}^3)$ (separation with regard to particles) and $\hat{\mathrm{H}}_0$ has the form $\hat{\mathrm{H}}_0 = \hat{\mathrm{H}}_{01} \otimes 1 + 1 \otimes \hat{\mathrm{H}}_{02}$. $\hat{\mathrm{H}}_{01}$ and $\hat{\mathrm{H}}_{02}$ are copies of the operator $\hat{\mathrm{h}} = -\Delta/2 - 1/\mid \vec{r} - \vec{R}_a \mid -1/\mid \vec{r} - \vec{R}_b \mid$. The spectrum of $\hat{\mathrm{h}}$ includes R–depending discrete eigenvalues of finite multiplicity. By taking the Pauli principle into account and additionally the separation of the basis space due to space symmetry, the discrete spectrum of $\hat{\mathrm{H}}_0$ can easily be derived from the spectrum of $\hat{\mathrm{h}}$. After optimizing the constants α, β and the curve Γ according to [13, pages 170–172] for the ground state, we conclude with

$$\rho_{lb} = \left\{ \frac{4}{E_{02} - E_{01}} \left(1 + \sqrt{1 + \frac{E_{01} + E_{02}}{8}} \right) \right\}^{-1} \tag{3.7}$$

where E_{01} and E_{02} are the first and second eigenvalues (from below) of $\hat{\mathrm{H}}_0$. In the united atom limit ($\vec{R}_a = \vec{R}_b = 0$) we get with $E_{01} = -4.0$ and $E_{02} = -2.5$

$$\rho_{lb} = \frac{3}{8+2\sqrt{3}} \approx \frac{1}{3.82} \,. \tag{3.8}$$

Thus the perturbation expansion in $\kappa = 1/Z$ converges in the united atom limit at least for $Z \geq 3.82$. This is identical to the result of Kato for the He–atom $Z_{u.a.} = 2Z \geq 7.64$ [14].

For completeness we should also note that for the operator family

$$\hat{\mathrm{H}}(\kappa) = \hat{\mathrm{H}}_0 + \kappa\hat{\mathrm{H}}_I = -\sum_{i=1}^{N}\left(\frac{\Delta_i}{2} + \sum_{k=1}^{2}\frac{C_k}{\mid \vec{R}_k - \vec{r}_i}\right) + \kappa\frac{1}{2}\sum_{\substack{i=1\\ i\neq j}}^{N}\sum_{j=1}^{N}\frac{1}{\mid \vec{r}_i - \vec{r}_j \mid} \quad , \tag{3.9}$$

this procedure for ground states leads to the more general result

$$\rho_{lb} = \left\{\frac{N(N-1)(C_1+C_2)}{E_{02}-E_{01}}\left(1+\sqrt{1+\frac{E_{01}+E_{02}}{N(C_1+C_2)^2}}\right)\right\}^{-1} \quad . \tag{3.10}$$

The eigenvalue equation for $\hat{\mathrm{h}}$ separates in spheroidal coordinates. We computed the R–dependent spectrum of $\hat{\mathrm{h}}$ according to [11]. By the spectrum of $\hat{\mathrm{h}}$ the eigenvalues E_{01} and E_{02} of $\hat{\mathrm{H}}_0$ are available. E_{01} is characterized by the configuration $(1s\sigma_g)^2$; E_{02} for $R < 2.3$ by $(1s\sigma_g, 2s\sigma_g)$ and for $R > 2.3$ by $(2p\sigma_u)^2$ (see Figure 3.1a). The convergence radius according to (3.7) (see ρ in Figure 3.1b) drops to zero with increasing R, because E_{02} and E_{01} become nearly degenerate.

In the case of the united atom, much better lower bounds for the convergence radius are available. Kato [13, page 413] treats an expansion not in 1/Z but in $1/(Z-\sigma)$, where σ is a screening constant with $Z - \sigma > 0$. Using the relationship between the expansion in $1/(Z-\sigma)$ and in 1/Z, he can enlarge the lower bound for the convergence radius to $Z_{u.a.} > 4.1$. Further R. Ahlrichs [2] proved the convergence for $Z_{u.a.} > 1.98$ employing the lower energy bounds of N.W. Bazley [4]. On the basis of their numerical results, Baker *et al.* conclude convergence for $Z_{u.a.} > 0.92$.

A more realistic estimation for the exact convergence radius is given by $\rho_{extr.} = \rho_{lb} * 8.386$ (see ρ' in Figure 1b), because $\rho_{extr.}$ goes to the corresponding atomic value of Baker *et al.* [3] for $R \to 0$ and the R–dependency of the convergence radius is mainly determined by the spectrum of $\hat{\mathrm{H}}_0$. To derive inequality (3.3) we must use the (poor) lower bound of $\hat{\mathrm{H}}_0$ in the united atom limit and cannot consider the R–dependency of this lower bound, which would improve the convergence radius for R> 0. By this, we assume convergence at least for $Z > 1/\rho_{extr.}$. Therefore an 1/Z–expansion is assumed to

be possible for $Z = 1$ at least in the range $0 \leq R' < 1.7$ and for $Z = 2$ at least in the range $0 \leq R' < 2.9$. But it is clear that convergency can not be reached far beyond these ranges.

Another point, which must be mentioned here, is that we must distinguish between the convergence radius for the expansion of eigenvalues and eigenstates of an operator in L^2 and the convergence radius for the expansion of eigenvalues and eigenstates of the projection of this operator in a finite basis space. Even if we could derive the exact convergence radius in a mathematically strict way, we could not infer the same for our PVRR–expansion [1]. This is a general problem in quantum chemistry where analytical treatments are normally not possible. The algebraic singularities introduced through the restriction to a finite basis may reduce the radius of convergence in a way that analytical properties, like considerations of the variation principle, will be destroyed. But in the case of the 1/Z–expansion for the H_2 ground state it is clear that for $R \rightarrow \infty$ there is no chance for convergence of the PVRR–expansion (or any other) at all. Knowing this, we carefully compare the results of our 1/Z–expansions for different Z with the corresponding eigenvalues of the Z–depending matrix families (for which the variation principle is valid).

[1] Whereas (3.3) holds also in a finite basis space, in (3.6) the spectrum $\Sigma(\hat{H}_0)$ must be replaced by the spectrum of the projection of $\hat{H}_0$ into the finite basis space (see discussion in [2]).

4. Results of the PVRR–Expansion

For the Rayleigh–Schrödinger expansion of Ψ' and ϵ' (see (2.11)) in power series in $\kappa = 1/Z$

$$\Psi' = \sum_{\nu=0}^{\infty} \kappa^{\nu} \Phi_{\nu} \quad , \quad \epsilon' = \sum_{\nu=0}^{\infty} \kappa^{\nu} \epsilon_{\nu} \tag{4.1}$$

Φ_0, $\epsilon_0 = \langle \Phi_0 \mid \hat{\mathrm{H}}'_0 \mid \Phi_0 \rangle$ and $\epsilon_1 = \langle \Phi_0 \mid \hat{\mathrm{H}}'_1 \mid \Phi_0 \rangle$ can be computed exactly (see Section 3). Using only ϵ_0 and ϵ_1 we get total energies (see Figure 4.1a–c) for the first three molecules of the isoelectronic H_2 sequence (H_2, He_2^{2+} and Li_2^{4+}) which qualitatively agree with their completely different nature regarding chemical bonding: H_2 is bound, He_2^{2+} is semi–stable with regard to dissociation and Li_2^{4+} is repulsive. These results are very promising, but misleading also, because an extension of expansion (4.1) to higher orders will not converge for the whole R–range. Thus expansions to finite order may lead to acceptable results for the potential curve, whereas the expansion coefficients ϵ_n have no physical meaning at all. In general arbitrary results can be obtained by such non–convergent expansions.

This is also illustrated by the behavior of ϵ_1 for $R \to \infty$. Due to the Σ_g symmetry of the wave function, $\epsilon_1(R \to \infty)$ is the mean value of the corresponding ϵ_1 values of the atomic systems $\mathrm{H} + \mathrm{H}$ and $\mathrm{H}^- + \mathrm{H}^+$. Whereas the 1/Z–expansion for the separated atoms is exactly given by $Z^2\epsilon_0$ ($\epsilon_0 = -1.0$), the 1/Z–expansion for the molecular system leads to $\epsilon_1(R \to \infty) = 0.3125 \neq 0$. This "wrong" $\epsilon_1(R \to \infty)$ value must be compensated by higher order corrections, which is not possible for arbitrary Z.

Nevertheless we approximate the expansion (4.1) by an PVRR–expansion to 99th order in the range $0.2 \leq R' \leq 9.0$ ($\Delta R' = 0.2$). To map (2.11) onto the finite dimensional matrix equation (2.12) we use a (9s7p2d / 4s4p2d) gaussian basis set (see Table 4.1). Using the Slater exponents of McLean *et al.* [22] (optimalized for the H_2 ground state at various R–values) we multiply the exponents of the s– and (p,d)–functions of this basis by the factors 0.8638 and 0.22932, respectively. Such a scaled basis improves the CI–energies in the range $R' \geq 2.6$. The same is true for $R' \leq 0.8$ with factors 1.0658 and 1.1358 for the s– and (p,d)–sector, respectively. In all cases we present the results derived with the basis which leads to the lowest CI–energy.

By choosing the MRD–CI selection threshold $T = 0$, all single and double excitations of the ground state configuration were taken into account. For a two–electron system this corresponds to a full CI treatment. The dimensions of the resulting hamilton matrices are 300.

In Table 4.2 the coefficients $\tilde{\epsilon}_n$ of the PVRR–expansion up to $N \leq 9$ for selected R–values are given. The perturbational energies for H_2 $S_N = \sum_{i=0}^{N} \tilde{\epsilon}_i +$

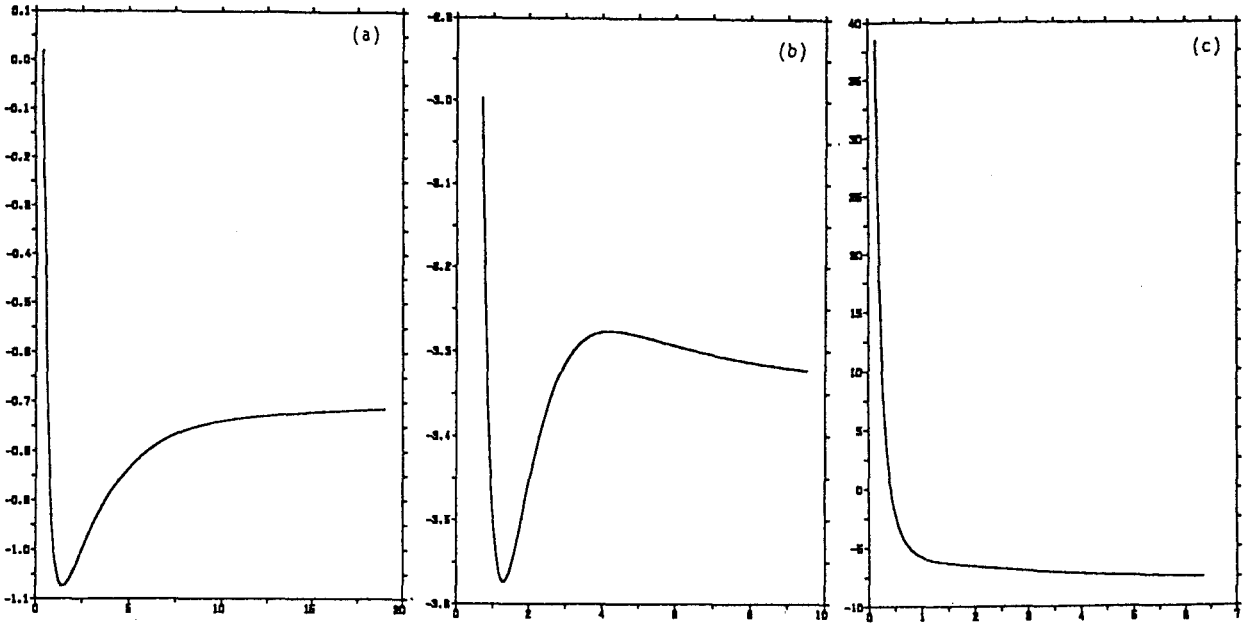

Figure 4.1: Sum of 0. and 1. order energies for the H_2–molecule [a], the He_2^{2+}–molecule[b] and the Li_2^{4+}–molecule [c].

$1/R'$ for odd N must be upper bounds for the total energy of H_2, as well as upper bounds for lowest eigenvalue of the matrix $\mathbf{H}_0 + \kappa \mathbf{H}_1 + 1/R'$ for $\kappa = 1$, denoted by $E_{\kappa=1}$. For the exact energies of H_2 [18, 19, 20] see E_{exact} in Table 4.2.

For low R' the PVRR–expansion converges rapidly. S_N is at least for $N \geq 11$ up to 7 significant digits identical to S_{99} and $E_{\kappa=1}$. This is valid in the range $R' \leq 2.4$. But the inequality

$$S_N \geq E_{\kappa=1} \qquad \text{for odd N} \tag{4.2}$$

holds only in the range $R' \leq 1.2$. For $R' = 1.4$ S_5 lies below $E_{\kappa=1}$ (but still above E_{exact}). This is inconsistent with the variational principle (in a finite basis space). The difference $E_{\kappa=1} - S_5$ grows with increasing R', and for $R' = 2.8$ S_5 for the first time lies below the exact energy. The perturbational energy to 99th order differs from $E_{\kappa=1}$ and at $R' = 3.6$ S_{99} has the astronomic value $5.1 \cdot 10^7$. This behavior grows stronger with increasing R'.

Table 4.1: **Gaussian basis set for H**

type	exponent ζ_i	coefficient C_i
s	837.22	0.000112
	123.524	0.000895
	27.7042	0.004737
	7.82599	0.019518
	2.56504	0.065862
	0.938258	0.178008
s	0.372145	1.0
s	0.155838	1.0
s	0.06618	1.0
p	18.880715	0.0000046
	5.191478	0.0000392
	1.761748	0.0002179
	0.736447	0.0007384
p	2.1175	1.0
p	0.77	1.0
p	0.28	1.0
d	2.3829	1.0
d	0.70655	1.0

Table 4.2: **Results of the PVRR–expansion at selected points**

	$R' = 0.2$	$R' = 0.8$	$R' = 1.4$	$R' = 2.0$	$R' = 2.8$	$R' = 3.6$
$\tilde{\epsilon}_0$	-3.856013	-3.108913	-2.568520	-2.205231	-1.882868	-1.670534
$\tilde{\epsilon}_1$	1.202149	0.956888	0.780827	0.661494	0.554065	0.482969
$\tilde{\epsilon}_2$	-0.149048	-0.122148	-0.108939	-0.107723	-0.126848	-0.184893
$\tilde{\epsilon}_3$	0.002712	0.005140	0.009003	0.014986	0.031234	0.073006
S_3	2.199800	-1.019033	-1.173343	-1.136474	-1.067275	-1.021675
$\tilde{\epsilon}_4$	0.000166	-0.000036	-0.000199	-0.000423	0.000063	0.024085
$\tilde{\epsilon}_5$	-0.000157	-0.000166	-0.000251	-0.000604	-0.003801	-0.045264
S_5	2.199810	-1.019236	-1.173794	-1.137500	-1.071013	-1.042854
$\tilde{\epsilon}_6$	-0.000037	-0.000008	0.000013	0.000081	0.000817	-0.003633
$\tilde{\epsilon}_7$	-0.000007	-0.000002	-0.000001	0.000032	0.000634	0.042787
S_7	2.199765	-1.019246	-1.137388	-1.137388	-1.069561	-1.037000
$\tilde{\epsilon}_8$	-0.000003	-0.000004	-0.000004	-0.000011	-0.000378	-0.014184
$\tilde{\epsilon}_9$	-0.000001	-0.000002	-0.000000	-0.000001	-0.000061	-0.040428
S_9	2.199761	-1.019252	-1.173785	-1.137400	-1.085051	-1.058313
S_{11}	2.199760	-1.019252	-1.173785	-1.137399	-1.069895	-0.991378
S_{99}	2.199760	-1.019252	-1.173785	-1.137399	-1.069911	$5.1 \cdot 10^7$
$E_{\kappa=1}$	2.199760	-1.019252	-1.173785	-1.137398	-1.070100	-1.027706
E_{exact}	—	-1.020056	-1.174474	-1.138132	-1.070681	-1.028045

5. Conclusion

First of all, it is clear that the 1/Z–expansion for the H_2 ground state does not converge for R$\rightarrow \infty$. This is substantiated by the radius of convergence given in Section 3 and illustrated by the results of the PVRR–expansion. The behavior of the ϵ_n for large n is strongly affected by the used basis space. Nevertheless the analytical behavior of the PVRR–expansions at different R'–values corresponds quite well to the extrapolated convergence radius $\rho_{extr.}$. Convergence of the PVRR–expansion to the 99th order can be achieved for small R–values ($R' \leq 2.4$). But already at $R' \geq 1.4$ the behavior of perturbational energy–sums to small orders shows that inferences of the variational principle are not longer valid. This indicates that algebraic singularities of $\tilde{\epsilon}'(Z)$ (see eq. (12)) reduce the radius of convergence. By $\rho_{extr.}$ we assume convergency at least for $R' \leq 1.7$.

Following this, the basic condition that 1/Z–expansions (as in the atomic He–atom case) converge for all Z–values of physical interest does not hold. Furthermore the used basis affects the radius of convergence. Only in case convergence can be proved in a mathematically strict way and error bounds for the $\tilde{\epsilon}_n$ can be given to exclude basis effects, a protection from misleading results is given. Because this is seldom possible, we would recommend at least to check the results in a way we do.

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