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Error bounds for the nonrelativistic electronic ground state energy of molecular hydrogen

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Upper and lower bounds are calculated for the nonrelativistic electronic ground state energy of the $^1\Sigma_g^+$ state of molecular hydrogen using the method of variance minimization with Hylleraas-CI functions. In order to solve the occurring new integrals centered interparticle coordinates were introduced.

1. Introduction

Since the basic work of Heitler and London [1] many authors have obtained increasingly accurate upper bounds for the nonrelativistic electronic ground state energy of the H_2 molecule, e.g. [2–4], within and beyond the Born–Opperheimer approximation. All these upper bounds were calculated using the Rayleigh–Ritz variational principle. In order to test the accuracy of the obtained energy values these values were compared with experimental data [5–8].

With the method of variance minimization [9–12] it is possible to calculate simultaneously upper and lower bounds for eigenvalues and hence exact error bounds are available. This procedure was used successfully – spectroscopic accuracy was achieved – for several states of the hydrogen molecule ion and its symmetric and unsymmetric isotopes even in non-Born–Oppenheimer calculations [13,14]. In this article we show that such calculations can also be expanded to four-body systems like H_2.

Let $\mathcal{H}$ be a selfadjoint operator with a discrete spectrum $\sigma_D = \{E_i | E_0 < E_1 < E_2 \ldots\}$ below the bottom of the continuum and domain $D_{\mathcal{H}}$. From Temple's formula [15]

$$E_n \geqslant (\mathcal{H}\Psi, \Psi) - \frac{(\mathcal{H}\Psi, \mathcal{H}\Psi) - (\mathcal{H}\Psi, \Psi)^2}{\rho - (\mathcal{H}\Psi, \Psi)}, \tag{1}$$

with $E_n \leqslant \rho \leqslant E_{n+1}$ and $(\Psi, \Psi)^2 = 1$, it can be seen [9–12] that a crucial point for the determination of a good lower bound is the minimization of the variance

$$F[\Psi] = (\mathcal{H}\Psi, \mathcal{H}\Psi) - (\mathcal{H}\Psi, \Psi)^2 . \tag{2}$$

If a n-dimensional vectorspace V_n is chosen with a basic $\{\varphi_i\}$ then Ψ is given by

$$\Psi = \sum_{i=1}^{n} c_i \varphi_i \tag{3}$$

and the minimization of the variance $F[\Psi]$ is equivalent [10–12] to the minimization of the Rayleigh quotient

$$\mathbf{R}[\lambda^*, \Psi] = \frac{\|(\mathcal{H} - \lambda^*)\Psi\|^2}{(\Psi, \Psi)} . \tag{4}$$

As is shown in [9–12] the minimum value for $F[\Psi]$ is obtained by an iteration procedure for both λ^* and Ψ.

2. Hamiltonian and basic functions

2.1. EXPANSIONS FOR r_{ij}^{-2}

In addition to those matrices necessary for upper bounds calculations the calculation of error intervals demands the calculation of matrix elements $H_{kl}^2 = (\mathcal{H}\phi_k, \mathcal{H}\phi_l)$. This leads to new types of integrals containing particle interaction terms down to the second negative power.

Their solution requires an expansion of the interaction terms r_{ij}^{-2} in series of the variables of integration. These expansions have to satisfy high requirements concerning the speed and the stability of convergence, especially in view of the desired high accuracy, which demands the calculation of a large number of integrals.

In this work two relations for r_{ij}^{-2} were used:

- the series expansion derived by Steinborn and Filter [16],

$$\frac{1}{r_{ij}^2} = \frac{1}{r_>^2} \sum_{l=0}^{\infty} \sum_{j=l}^{\infty}{}^{(2)} (2l+1) \frac{(j-l-1)!!}{(j-l)!!} \frac{(j+l)!!}{(j+l+1)!!} \left(\frac{r_<}{r_>}\right)^j P_l(\cos\vartheta) \tag{5}$$

  with $\sum_{j=l}^{\infty}{}^{(2)} \ldots$ indicating that the summation over j proceeds in steps of two,
- and the one by Lüchow and Kleindienst [17],

$$\frac{1}{r_{ij}^2} = \sum_{q=0}^{\infty} \left\{ \ln \left| \frac{r_i + r_j}{r_i - r_j} \right| \sum_{\lambda=0}^{q} C_{q,\lambda} r_i^{q-2\lambda-1} r_j^{-q+2\lambda-1} - \sum_{\lambda=0}^{q-1} C'_{q,\lambda} r_i^{q-2\lambda-2} r_j^{-q+2\lambda} \right\} P_q(\cos\vartheta) \tag{6}$$

with

$$C'_{q,\lambda} = C'_{q,q-\lambda} \quad \text{and} \quad C_{q,\lambda} = C_{q,q-\lambda-1}\,,$$

$$C_{q+1,\lambda} = \begin{cases} \dfrac{2q+3}{2q+2} C_{q,0}\,, & \lambda = 0, \lambda = q+1\,, \\ \dfrac{2q+3}{2q+2}\left(C_{q,\lambda} + C_{q,\lambda-1} - \dfrac{2q}{2q-1} C_{q-1,\lambda-1}\right), & 1 \leqslant \lambda \leqslant q\,, \end{cases} \tag{7}$$

$$C'_{q+1,\lambda} = \begin{cases} \dfrac{2q+3}{2q+2} C'_{q,0}\,, & \lambda = 0, \lambda = q\,, \\ \dfrac{2q+3}{2q+2}\left(C'_{q,\lambda} + C_{q,\lambda-1} - \dfrac{2q}{2q-1} C'_{q-1,\lambda-1}\right), & 1 \leqslant \lambda \leqslant q-1\,, \end{cases} \tag{8}$$

($C_{0,0} = \frac{1}{2}$ and $C'_{1,0} = \frac{3}{2}$).

2.2. THE CHOICE OF THE COORDINATE SYSTEM

Highly accurate calculations of upper bounds for the electronic ground state of molecular hydrogen like those published by Bishop and Cheung [3] or Kolos et al. [4] were performed using basic functions in confocal elliptic coordinates.

These coordinates are suitable for H_2^+ and its isotopes but fail for H_2 because of bad numeric properties of the expansion r_{ij}^{-2} in elliptic coordinates [18].

In order to apply the stable expansions (5) and (6) basic functions $\phi_i(1,2)$ were chosen in interparticle coordinates,

$$\phi_i(1,2) = r_{A1}^{k_i} r_{A2}^{l_i} r_{B1}^{m_i} r_{B2}^{n_i} r_{12}^{p_i} e^{-\alpha(r_{A1}+r_{A2})} \tag{9}$$

with one nucleus (A) at the centre of the coordinate system and the other at position $(0,0,R)$. Because of this the r_{Ai} are in the following denoted by r_i.

The Born–Oppenheimer Hamiltonian (in atomic units) was used in the form derived by Frost [19]:

$$\begin{aligned} \mathcal{H} = \mathcal{T} + \mathcal{V} = &-\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1}\right) - \frac{1}{2}\left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2}\right) \\ &- \frac{1}{2}\left(\frac{\partial^2}{\partial r_{B1}^2} + \frac{2}{r_{B1}}\frac{\partial}{\partial r_{B1}}\right) - \frac{1}{2}\left(\frac{\partial^2}{\partial r_{B2}^2} + \frac{2}{r_{B2}}\frac{\partial}{\partial r_{B2}}\right) \\ &- \left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\right) \\ &- \frac{r_1^2 + r_{B1}^2 - R^2}{2 r_1 r_{B1}} \frac{\partial^2}{\partial r_1 \partial r_{B1}} - \frac{r_2^2 + r_{B2}^2 - R^2}{2 r_2 r_{B2}} \frac{\partial^2}{\partial r_2 \partial r_{B2}} \end{aligned}$$

$$-\frac{r_1^2+r_{12}^2-r_2^2}{2r_1r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}}-\frac{r_2^2+r_{12}^2-r_1^2}{2r_2r_{12}}\frac{\partial^2}{\partial r_2\partial r_{12}}$$
$$-\frac{r_{B1}^2+r_{12}^2-r_{B2}^2}{2r_{B1}r_{12}}\frac{\partial^2}{\partial r_{B1}\partial r_{12}}-\frac{r_{B2}^2+r_{12}^2-r_{B1}^2}{2r_{B2}r_{12}}\frac{\partial^2}{\partial r_{B2}\partial r_{12}}$$
$$-\frac{1}{r_1}-\frac{1}{r_2}-\frac{1}{r_{B1}}-\frac{1}{r_{B2}}+\frac{1}{r_{12}}+\frac{1}{R}\,. \tag{10}$$

2.3. CLASSIFICATION OF BASIS SETS

In analogy to Hylleraas-CI calculations performed on the Li-atom [20] the following classes of basis sets can be formed:

unlinked basis sets	consisting of functions with only one correlation term r_{12}^n or "pseudo"-correlation term $r_{B_i}^m$.
first order linked basis sets	consisting of functions not containing the expression $r_{Bi}r_{12}$;
second order linked basis sets	consisting of functions containing the expression $r_{Bi}r_{12}$; with the power of r_{B_j} even;
fully linked basis sets	consisting of arbitrary functions.

The meaning of this classification is to avoid new and complicated integral expressions in the calculation of the variance, esp. integrals, containing terms $(1/r_{Bi}^2)(1/r_{12}^2)$. Later it will be shown that these integrals do not occur if basis sets of the unlinked or first order linked class are chosen. For second order linked basis sets these integrals occur but can be solved with sufficient accuracy.

In order to reduce the dimension of the variational space an algorithm for the selection of basic functions was designed in analogy to the process described by Bishop and Cheung [3]:

A function φ_i is selected if

1. the power p_i of r_{12} applies to $0 \leqslant p_i \leqslant 3$,
2. the powers k_i, l_i, m_i and n_i of r_1, r_2, r_{B1} and r_{B2} apply to

$$k_i + m_i \leqslant a[p_i] \quad \text{and} \quad l_i + n_i \leqslant a\,, \quad a = a[p_i] \in \mathbf{N}_0\,,$$

$$k_i + l_i + m_i + n_i \leqslant b \in \mathbf{N}_0\,,$$

3. and $k_i, l_i \leqslant k_{max}, m_i, n_i \leqslant m_{max}$.

A basis sets $\{\phi_i\}$ can then be characterized by the following notation:

$$\text{class } (a[0], a[1], a[2], a[3]/b)_{k_{max}, m_{max}}\,.$$

For the maximum values of $a[p_i]$, b, k_{max} and m_{max} chosen within this work see tables 2 and 3.

3. Integral solutions

3.1. INTEGRALS FOR UPPER BOUND CALCULATIONS

The determination of upper bounds for energy eigenvalues requires the calculation of matrix elements $H_{ij} = (\mathcal{H}\phi_i, \phi_i)$ and $S_{ij} = (\phi_i, \phi_j)$. They are linear combinations of integrals of the form

$$I_1(k,l,m,n,p) = \int r_1^k r_2^l r_{B1}^m r_{B2}^n r_{12}^p e^{-2\alpha(r_1+r_2)}\, d\tau \tag{11}$$

with boundary conditions

$$k,l,m,n,p \geqslant -1\,,$$

$$k+l \geqslant -1\,, \quad m+n \geqslant -1\,, \quad k+n \geqslant -1\,, \quad l+m \geqslant -1\,,$$

$$k+m \geqslant -2\,, \quad l+n \geqslant -2\,, \quad k,l,m,n \geqslant -2-p\,,$$

resulting from the application of the Hamiltonian (10) on an arbitrary basic function ϕ_i.

Expressing $d\tau$ in special coordinates,

$$d\tau = r_1^2 r_2^2 \sin\vartheta_1 \sin\vartheta_2\, d\varphi_1 d\varphi_2 d\vartheta_1 d\vartheta_2 dr_1 dr_2\,,$$

leads to

$$I_1(k,l,m,n,p) = \int_0^\infty \int_0^\infty \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} r_1^{k+2} r_2^{l+2} r_{B1}^m r_{B2}^n r_{12}^p e^{-2\alpha(r_1+r_2)} \times \sin\vartheta_1 \sin\vartheta_2\, d\varphi_1 d\varphi_2 d\vartheta_1 d\vartheta_2 dr_1 dr_2\,. \tag{12}$$

This integral can be solved by expanding the terms r_{B1}^m, r_{B2}^n and r_{12}^p in a series expansion derived by Perkins [21]:

$$r_{ij}^\nu = \sum_{q=0}^{L_1} P_q(\cos\vartheta_{ij}) \sum_{k=0}^{L_2} C_{\nu,q,k} s_{ij}^{q+2k} g_{ij}^{\nu-q-2k} \quad (\nu \geqslant -1) \tag{13}$$

with

$$L_1 = \begin{cases} \dfrac{\nu}{2} : & mod(\nu,2) = 0\,, \\ \infty : & mod(\nu,2) \neq 0\,, \end{cases}$$

$$L_2 = \begin{cases} \dfrac{\nu}{2} - q \;:\; mod(\nu,2) = 0\,, \\ \dfrac{\nu+1}{2} \;:\; mod(\nu,2) \neq 0\,, \end{cases}$$

and

$$C_{\nu,q,k} = \frac{2q+1}{\nu+2}\binom{\nu+2}{2k+1}\prod_{t=0}^{\tau}\frac{2k+2t-\nu}{2k+2q-2t+1}$$

with $\tau = min[q-1, (\nu+1)/2]$.

Substituting the expression for r_{12}^{-1} from eq. (13) into eq. (12) and integrating with respect to the angular coordinates leads to

$$\begin{aligned} I_1(k,l,m,n,p) = 16\pi^2 \sum_{q=0}^{L_1} \frac{1}{(2q+1)^2} \sum_{\rho=0}^{L_{21}} \sum_{\mu=0}^{L_{22}} \sum_{\nu=0}^{L_{23}} C_{m,q,\mu} C_{n,q,\nu} C_{p,q,\rho} \\ \times \Bigg\{ R^{m+n-2(q+\mu+\nu)} \Bigg[\int_0^R \int_0^{r_2} r_1^{k+2(q+\mu+\rho+1)} r_2^{l+p+2(\nu-\rho+1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \\ + \int_0^R \int_{r_2}^R r_1^{k+p+2(\mu-\rho+1)} r_2^{l+2(q+\nu+\rho+1)} e^{-2\alpha(r_1+r_2)} dr_1 dr_2 \Bigg] \\ + R^{m+2(\nu-\mu)} \int_R^\infty \int_0^R r_1^{k+2(q+\mu+\rho+1)} r_2^{l+p+n-2(q+\nu+\rho-1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \\ + R^{n+2(\mu-\nu)} \int_0^R \int_R^\infty r_1^{k+p+m-2(q+\mu+\rho-1)} r_2^{l+2(q+\nu+\rho+1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \\ + R^{2(q+\mu+\nu)} \Bigg[\int_R^\infty \int_R^{r_2} r_1^{k+m+2(\rho-\mu+1)} r_2^{l+n+p-2(q+\nu+\rho-1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \\ + \int_R^\infty \int_{r_2}^\infty r_1^{k+m+p-2(q+\mu+\rho-1)} r_2^{l+n+2(\rho-\nu+1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \Bigg] \Bigg\}. \end{aligned} \tag{14}$$

Solutions for the auxiliary integrals are given in the appendix.

Due to the following identities only three types of integrals have to be solved.

$$V_{11}(r_1,r_2) = \int_0^R \int_0^{r_2} F(r_1,r_2)\, dr_1 dr_2 = \int_0^R \int_{r_2}^R F(r_2,r_1)\, dr_1 dr_2 = V_{12}(r_2,r_1)\,, \tag{15}$$

$$V_{13}(r_1,r_2) = \int_R^\infty \int_0^R F(r_1,r_2)\, dr_1 dr_2 = \int_0^R \int_R^\infty F(r_2,r_1)\, dr_1 dr_2 = V_{14}(r_2,r_1)\,, \tag{16}$$

$$V_{15}(r_1,r_2)=\int_R^\infty\int_R^{r_2}F(r_1,r_2)\,dr_1dr_2=\int_R^\infty\int_{r_2}^\infty F(r_2,r_1)\,dr_1dr_2=V_{16}(r_2,r_1)\,. \tag{17}$$

3.2. INTEGRALS FOR THE MINIMIZATION OF THE VARIANCE

Performing calculations with the method of variance minimization leads to new integral types in addition to those needed for upper bound calculations:

Integrals containing one factor r_{12}^{-2}:

$$I_2(k,l,m,n)=\int r_1^k r_2^l r_{B1}^m r_{B2}^n \frac{1}{r_{12}^2}e^{-2\alpha(r_1+r_2)}\,d\tau\,;$$

integrals containing one factor r_{Bi}^{-2}:

$$I_3(k,l,m,p)=\int r_1^k r_2^l r_{Bj}^m r_{12}^p \frac{1}{r_{Bi}^2}e^{-2\alpha(r_1+r_2)}\,d\tau\quad(i,j=1,2)\,;$$

and integrals containing two interparticle coordinates to the second negative power:

$$I_4(k,l,m)=\int r_1^k r_2^l r_{Bi}^m \frac{1}{r_{Bj}^2}\frac{1}{r_{12}^2}e^{-2\alpha(r_1+r_2)}\,d\tau\quad(i,j=1,2)\,.$$

3.2.1. Solution of integrals of type I_2

The solution of integrals of the form

$$I_2(k,l,m,n)=\int r_1^k r_2^l r_{B1}^m r_{B2}^n \frac{1}{r_{12}^2}e^{-2\alpha(r_1+r_2)}\,d\tau \tag{18}$$

with $k,l\geqslant -2, k+l\geqslant -2$ and $m,n\geqslant -1, k+l+m+n>0$ is achieved by expanding r_{Bi}-terms in a series according to Perkins (eq. (13)) and for the r_{12}^{-2} term applying eq. (6).

Integration with respect to the angular coordinates yields

$$\begin{aligned}
&I_2(k,l,m,n)\\
&=\sum_{q=0}^{L_1}\frac{1}{(2q+1)^2}\left\{\sum_{\nu=0}^{L_{21}}\sum_{\mu=0}^{L_{22}}D_{n,q,\nu}D_{m,q,\mu}\left[\sum_{\lambda=0}^{q}C_{q,\lambda}\right.\right.\\
&\quad\times R^{m+n-2(q+\mu+\nu)}\int_0^R\int_0^R\ln\left|\frac{r_1+r_2}{r_1-r_2}\right|r_1^{k+2+2(q-\lambda+\mu)}r_2^{l+2(\lambda+\nu)+1}e^{-2\alpha(r_1+r_2)}\,dr_1dr_2\\
&\quad\left.+R^{n+2(\mu-\nu)}\int_0^R\int_R^\infty\ln\left|\frac{r_1+r_2}{r_1-r_2}\right|r_1^{k+m-2(\lambda+\mu)+2}r_2^{l+2(\lambda+\nu)+1}e^{-2\alpha(r_1+r_2)}\,dr_1dr_2\right.
\end{aligned}$$

$$+ R^{m+2(\nu-\mu)} \int_R^\infty \int_0^R \ln \left| \frac{r_1 + r_2}{r_1 - r_2} \right| r_1^{k+2+2(q-\lambda+\mu)} r_2^{l+n-2(q-\lambda+\nu)+1} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2$$

$$+ R^{2(q+\mu+\nu)} \int_R^\infty \int_R^\infty \ln \left| \frac{r_1 + r_2}{r_1 - r_2} \right| r_1^{k+m-2(\lambda+\mu)+2} r_2^{l+n-2(q-\lambda+\nu)+1} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \Bigg)$$

$$- \sum_{\lambda=0}^{q} C'_{q,\lambda}$$

$$\times \Bigg(R^{m+n-2(q+\mu+\nu)} \int_0^R \int_0^R r_1^{k+2(q-\lambda+\mu)} r_2^{l+2(\lambda+\nu)+2} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2$$

$$+ R^{n+2(\mu-\nu)} \int_0^R \int_R^\infty r_1^{k+m-2(\lambda+\mu)} r_2^{l+2(\lambda+\nu)+2} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2$$

$$+ R^{m+2(\nu-\mu)} \int_R^\infty \int_0^R r_1^{k+2(q-\lambda+\mu)} r_2^{l+n-2(q-\lambda+\nu-1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2$$

$$+ R^{2(q+\mu+\nu)} \int_R^\infty \int_R^\infty r_1^{k+m-2(\lambda+\mu)} r_2^{l+n-2(q-\lambda+\nu-1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \Bigg) \Bigg] \Bigg\} \quad (19)$$

with

- $D_{n,q,\nu}$: coefficients of the expansion by Perkins
- $C_{q,\lambda}$, $C'_{q,\lambda}$: coefficients of the expansion by Lüchow;
- $P_q(\cos\vartheta)$: Legendre polynomials;
- L_1, L_{21}, L_{22} : boundary conditions of summation (see eq. (13)).

3.2.2. Solution of integrals of type I_3

Integrals of the type

$$I_3(k,l,n,p) = I_3(l,k,n,p)$$

$$= \int r_1^k r_2^l \frac{1}{r_{B1}^2} r_{B2}^n r_{12}^p e^{-2\alpha(r_1+r_2)}\, d\tau$$

$$= \int r_1^l r_2^k \frac{1}{r_{B2}^2} r_{B1}^n r_{12}^p e^{-2\alpha(r_1+r_2)}\, d\tau \quad (20)$$

with $n, p \geqslant -1$ can be solved in analogy to I_2.

With the expansions of Perkins and Lüchow and the notation in eq. (19) integration with respect to the angular coordinates leads to

$$
\begin{aligned}
I_3(k,l,n,p) = \sum_{q=0}^{L_1} \frac{16\pi^2}{(2q+1)^2} \sum_{\nu=0}^{L_{21}} \sum_{\mu=0}^{L_{22}} D_{n,q,\nu} D_{p,q,\mu} \Bigg\{ \sum_{\lambda=0}^{q} C_{q,\lambda} \Bigg[R^{2(\lambda+\nu)-1} \\
\times \left(\int_R^\infty \int_0^{r_2} \ln \left| \frac{r_1+R}{r_1-R} \right| r_1^{k+2(q+\mu-\lambda)+1} r_2^{l+n+p-2(q+\mu+\nu-1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \right. \\
\left. + \int_R^\infty \int_{r_2}^\infty \ln \left| \frac{r_1+R}{r_1-R} \right| r_1^{k+p-2(\mu+\lambda)+1} r_2^{l+n+2(\mu-\nu+1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \right) \\
+ R^{n-2(q+\nu-\lambda)-1} \left(\int_0^R \int_0^{r_2} \ln \left| \frac{r_1+R}{r_1-R} \right| r_1^{k+2(q+\mu-\lambda)+1} r_2^{l+p+2(\nu-\mu+1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \right. \\
\left. + \int_0^R \int_{r_2}^\infty \ln \left| \frac{r_1+R}{r_1-R} \right| r_1^{k+p-2(\mu+\lambda)+1} r_2^{l+2(q+\nu+\mu+1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \right) \Bigg] \\
- \sum_{\lambda=0}^{q-1} C'_{q,\lambda} \Bigg[R^{2(\lambda+\nu)} \left(\int_R^\infty \int_0^{r_2} r_1^{k+2(q+\mu-\lambda)} r_2^{l+n+p-2(q+\mu+\nu-1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \right. \\
\left. + \int_R^\infty \int_{r_2}^\infty r_1^{k+p-2(\mu+\lambda)} r_2^{l+n+2(\mu-\nu+1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \right) \\
+ R^{n-2(q+\nu-\lambda)} \left(\int_0^R \int_0^{r_2} r_1^{k+2(q+\mu-\lambda)} r_2^{l+p+2(\nu-\mu+1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \right. \\
\left. + \int_0^R \int_{r_2}^\infty r_1^{k+p-2(\mu+\lambda)} r_2^{l+2(q+\nu+\mu+1)} e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \right) \Bigg] \Bigg\} . \qquad (21)
\end{aligned}
$$

3.2.3. Solution of integrals of type I_4

Integrals containing products $r_{Bi}^{-2} r_{12}^{-2}$ (with $i = 1, 2$) cannot be solved using eq. (6) twice because this leads to auxiliary integrals which are divergent although the total integral is finite.

This problem can be avoided by dividing the domain of integration into two parts:

$$
\begin{aligned}
I_4(k,l,m) &= \int_0^\infty \int_0^\epsilon \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} r_1^k r_2^l r_{B1}^m \frac{1}{r_{B2}^2} \frac{1}{r_{12}^2} e^{-2\alpha(r_1+r_2)}\, d\tau \\
&\quad + \int_0^\infty \int_\epsilon^\infty \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} r_1^k r_2^l r_{B1}^m \frac{1}{r_{B2}^2} \frac{1}{r_{12}^2} e^{-2\alpha(r_1+r_2)}\, d\tau \\
&= I_{41}(k,l,m) + I_{42}(k,l,m) , \\
d\tau &= r_1^2 r_2^2 \sin\vartheta_1 \sin\vartheta_2\, d\varphi_1 d\varphi_2 d\vartheta_1 d\vartheta_2 dr_2 dr_1 \qquad (22)
\end{aligned}
$$

with ϵ as small as possible.

For the first part eq. (6) can be used twice while for the second part the expansion by Steinborn and Filter as well as the expansion by Lüchow and Kleindienst is used. The third term r_{Bj}^m with $m \geqslant -1$ in both cases is treated by the ansatz of Perkins. Because of the symmetry of the integral I_4 with respect to the electron coordinates, it is sufficient to treat only one of the cases, e.g. $r_{B1}^m r_{B2}^{-2} r_{12}^{-2}$. (1-2)-interchange leads to the other case, $r_{B2}^n r_{B1}^{-2} r_{12}^{-2}$.

Tests proved $\epsilon = 0.5$ to be the smallest possible value; a calculation of certain auxiliary integrals with even smaller values of ϵ led to numerical instabilities.

Considering the expansion by Steinborn and Filter (eq. (5)) the advantage of the basis sets of *second order linked* class in comparison to the *fully linked* basis set becomes obvious:

Expanding r_{B2}^{-2} according to eq. (5), r_{12}^{-2} using eq. (6), r_{B1}^m according to eq. (14) and integrating with respect to the angular coordinates results in

$$
\begin{aligned}
I_{41}(k,l,m) = & \sum_{q=0}^{\frac{m}{2}} \frac{16\pi^2}{2q+1} \sum_{\mu=0}^{\frac{m}{2}-q} D_{m,q,\mu} \\
& \times \sum_{j=q}^{\infty}{}^{(2)} \frac{(j-q-1)!!(j+q)!!}{(j-q)!!(j+q+1)!!} R^{m-j-q-2\mu-2} \Bigg\{ \sum_{\lambda=0}^{q} C_{q,\lambda} \\
& \times \int_0^{\infty} \int_0^{\epsilon} \ln \left| \frac{r_1+r_2}{r_1-r_2} \right| r_1^{k+2(q-\lambda+\mu)+1} r_2^{l+j-q+2\lambda+1} e^{-2\alpha(r_1+r_2)} \, dr_2 dr_1 \\
& - \sum_{\lambda=0}^{q-1} C'_{q,\lambda} \int_0^{\infty} \int_0^{\epsilon} r_1^{k+2(q-\lambda+\mu)} r_2^{l+j-q+2\lambda+2} e^{-2\alpha(r_1+r_2)} \, dr_2 dr_1 \Bigg\} \qquad (23)
\end{aligned}
$$

if only *second order linked* functions are used, because

- for small ϵ we have $r_2 < R$;
- for even m there is no distinction of cases in the expansion by Perkins;
- for even m the expansion finishes at $q = m/2$.

Hence the two main disadvantages of the Steinborn expansion can be avoided:

- the series converges rapidly, because $\frac{r_<}{r_>} < 1$;
- the q-summation finishes exactly for $q = m/2$ and so the double infinite summation is removed.

Applying the expansion by Lüchow and Kleindienst twice and performing the integration of I_{42} with respect to the angular coordinates leads to

$$
\begin{aligned}
I_{42}(k,l,m) = \sum_{q=0}^{\frac{m}{2}} \frac{16\pi^2}{(2q+1)^2} \sum_{\mu=0}^{\frac{m}{2}-q} D_{m,q,\mu} \Bigg(& \sum_{\lambda=0}^{q} \sum_{\nu=0}^{q} C_{q,\lambda} C_{q,\nu} R^{m-2(q-\lambda+\mu)-1} \\
& \times \int_0^\infty \int_\epsilon^\infty \ln \left| \frac{r_1 + r_2}{r_1 - r_2} \right| \ln \left| \frac{r_2 + R}{r_2 - R} \right| r_1^{k+1+2(q+\mu-\nu)} r_2^{l+2(\nu-\lambda)} e^{-2\alpha(r_1+r_2)} \, dr_2 dr_1 \\
& - \sum_{\lambda=0}^{q} \sum_{\nu=0}^{q-1} C_{q,\lambda} C'_{q,\nu} R^{m-2(q-\lambda+\mu)-1} \\
& \times \int_0^\infty \int_\epsilon^\infty \ln \left| \frac{r_2 + R}{r_2 - R} \right| r_1^{k+2(q+\mu-\nu)} r_2^{l+2(\nu-\lambda)+1} e^{-2\alpha(r_1+r_2)} \, dr_2 dr_1 \\
& - \sum_{\lambda=0}^{q-1} \sum_{\nu=0}^{q} C'_{q,\lambda} C_{q,\nu} R^{m-2(q-\lambda+\mu)} \\
& \times \int_0^\infty \int_\epsilon^\infty \ln \left| \frac{r_1 + r_2}{r_1 - r_2} \right| r_1^{k+2(q+\mu-\nu)+1} r_2^{l+2(\nu-\lambda)} e^{-2\alpha(r_1+r_2)} \, dr_2 dr_1 \\
& + \sum_{\lambda=0}^{q-1} \sum_{\nu=0}^{q-1} C'_{q,\lambda} C'_{q,\nu} R^{m-2(q-\lambda+\mu)} \\
& \times \int_0^\infty \int_\epsilon^\infty r_1^{k+2(q+\mu-\nu)} r_2^{l+2(\nu-\lambda)} e^{-2\alpha(r_1+r_2)} \, dr_2 dr_1 \Bigg) . \qquad (24)
\end{aligned}
$$

Solutions for all occurring auxiliary integrals are given in the appendix.

4. Notes on computation

All programs were written in FORTRAN 77 and carried out on a CONVEX C210 vector computer using 64 bit arithmetics (REAL*8) for the integral routines. The auxiliary integrals were determined with at least 12 significant digits. Starting values for recursions were calculated numerically with the subroutine "CADRE" [22] based on the Romberg algorithm. In order to improve the convergence of the series for the determination of the total integrals ($I_1 - I_4$) the method of non linear convergence accelerators as described by Levin [23] was used.

Matrix eigenvalue computations were performed with a subroutine based on the Wielandt algorithm as described in [24]. For larger basis sets computations had to be performed with 128 bit arithmetics in order to avoid the occurring numerical instabilities (see below).

5. Results of upper bound calculations

Unless otherwise stated, all calculations published here were performed for an internuclear distance of $R = 1.4$ a.u.

After performing tests with "complete" basis sets of the different classes [#1] it became obvious that both *unlinked* and *first order linked* basis sets could not be used to achieve results for upper bounds with spectroscopic accuracy. Table 1 shows some of the results for complete basis sets with $n = 6$ and $n = 7$.

Table 1
Upper bounds of the electronic ground state energy obtained by complete basis sets of different classes.

Class	n	Dim	$E_0(R)$
unlinked	6	120	−1.162 599 851 529
	7	164	−1.162 628 780 295
first order linked	6	390	−1.174 461 608 879
	7	605	−1.174 471 815 471
second order linked	6	424	−1.174 467 901 176
	7	655	−1.174 474 590 160
fully linked	6	440	−1.174 469 271 176
	7	680	−1.174 475 189 053

The next step was to optimize the non-linear coefficient α. Calculating upper bounds for medium sized basis sets of *fully linked* class for different values of α in the interval $0.5 \leqslant \alpha \leqslant 2.0$ produced the optimum value being $\alpha = 1.4$, therefore all calculations were carried out with $\alpha = 1.4$.

The results in table 1 show that obviously a strategy for the selection of basis functions is needed in order to achieve spectroscopic accuracy. Optimized basis sets were constructed according to the method described by Bishop and Cheung [3] because of the similarity between the structures of their basis sets and those used in this work. Starting from a basis $(6, 4, 5, 3/6)_{6,6}$ the possible sum of the exponents was raised successively. The results shown in tables 2 and 3 indicate that spectroscopic accuracy can be achieved.

Table 2
Upper bounds for the ground state energy: *second order linked* basis sets.

Basis	Dimension	λ_R
$(6,4,5,3/6)_{6,6}$	340	−1.174 466 733
$(6,4,5,3/7)_{6,6}$	447	−1.174 473 765
$(6,4,5,3/8)_{6,6}$	559	−1.174 474 709
$(7,5,6,4/7)_{7,7}$	556	−1.174 474 377
$(7,5,6,4/8)_{7,7}$	740	−1.174 475 228
$(7,5,6,4/9)_{7,7}$	906	−1.174 475 433
$(8,6,7,5/9)_{8,8}$	1131	−1.174 475 467
$(8,6,7,5/10)_{8,8}$	1404	−1.174 475 570
$(8,6,7,5/12)_{8,8}$	1863	−1.174 475 652

[#1] A basis set of the form class $(n, n, n, n/n)_{n,n}$ shall in this context be called "complete".

Table 3
Upper bounds for the ground state energy: *fully linked* basis sets.

Basis	Dimension	λ_R
$(6,4,5,3/6)_{6,6}$	353	−1.174 468 866
$(6,4,5,3/7)_{6,6}$	463	−1.174 474 880
$(6,4,5,3/8)_{6,6}$	577	−1.174 475 352
$(7,5,6,4/7)_{7,7}$	578	−1.174 475 146
$(7,5,6,4/8)_{7,7}$	768	−1.174 475 590
$(7,5,6,4/9)_{7,7}$	938	−1.174 475 604
$(8,6,7,5/9)_{8,8}$	1173	−1.174 475 637
$(8,6,7,5/10)_{8,8}$	1453	−1.174 475 645
$(8,6,7,5/12)_{8,8}$	1920	−1.174 475 663

A comparison to previous results underlines the quality of basis sets in confocal elliptic coordinates (table 4).

Table 4
Comparison of results of calculations performed with functions in confocal elliptic coordinates. $R = 1.4$ a.u.

Authors	Dimension	E_0[a.u.]
Kolos et al. (1986)	249	−1.174 475 668
Bishop, Cheung (1978)	249	−1.174 475 65
This work	1920	−1.174 475 663

6. Results of error interval calculations

Error intervals were calculated for the nonrelativistic electronic ground state of molecular hydrogen. The internuclear distance was chosen $R = 1.4$ a.u.; the optimum non-linear parameter $\alpha = 1.4$ for upper bound calculation was used as well. Using the method of variance minimization in connection with Temple's formula to calculate a lower bound for the ground state E_0 a good lower bound ρ for the first excited state E_1 is required. A lower bound for E_1 can be obtained by performing a minimization of the variance F. With an upper bound for E_1 as a starting value for the iteration process this lower bound E_1^- can be obtained according to

$$E_1^- = \lambda^* - \sqrt{F}\,. \tag{25}$$

With a *second order linked* basis set $(7,5,6,4/9)_{7,7}$ containing 938 functions we calculated a lower bound for the first excited electronic state $\rho = -0.7164458704$, which we used for the calculation of lower bounds for the ground state with Temple's formula. The determination of error intervals with spectroscopic accu-

racy was performed with large basis sets of *second order linked* class. The selection of basis sets followed the method described by Bishop and Cheung, which successfully had been adopted for upper bound calculations. Our calculations showed that it was necessary to use basis sets with dimensions ~ 1000, which leads to serious stability problems in the numerical solution of the matrix eigenvalue problems. Hence all matrix elements had to be stored as REAL*16 variables with a size of 128 bits instead of 64 bits (REAL*8). Table 5 shows the result of these calculations.

Table 5
Upper, lower bounds and variances for the electronic ground state: *second order linked* basis sets.

Basis	Dim.	λ^*	E^-	F
$(6,4,5,3/6)_{6,6}$	340	−1.174 445 675	−1.175 007 900	2.574 989E-4
$(6,4,5,3/7)_{6,6}$	447	−1.174 447 211	−1.174 596 705	6.846 853E-5
$(6,4,5,3/8)_{6,6}$	559	−1.174 447 351	−1.174 534 182	3.976 877E-5
$(7,5,6,4/7)_{7,7}$	556	−1.174 447 240	−1.174 558 320	5.087 462E-5
$(8,6,7,5/8)_{8,8}$	869	−1.174 447 169	−1.174 487 634	1.853 305E-5
$(8,6,7,5/9)_{8,8}$	1131	−1.174 433 835	−1.174 458 385	1.124 374E-5

Calculations with larger basis sets were not performed because of numerical instabilities in calculating the necessary Rayleigh quotients. E.g., the basis set $(8,6,7,5/9)_{8,8}$ produced a lower bound lying *above* the upper bound obtained by the variation method. The reason for this is discussed below.

Combining the optimum result for a lower bound (basis set $(8,6,7,5/8)_{8,8}$) with the best upper bound, which is supplied by the Ritz method the nonrelativistic electronic ground state $^1\Sigma_g^+$ of molecular hydrogen can be determined to be

$$-1.174487634 \leqslant E_0 \leqslant -1.174475663$$

in atomic units, i.e. in spectroscopic units

$$38295.608\ \text{cm}^{-1} \leqslant D_e^{\infty}(H_2) \leqslant 38292.981\ \text{cm}^{-1}\,.$$

The error interval of 2.627 cm^{-1} is about six times larger than the experimental error published by McCormack and Eyler [8].

7. Examination of numerical instabilities

In this section the numerical instabilities in calculating Rayleigh quotients shall be discussed briefly.

7.1. LOSS OF SIGNIFICANCE IN CALCULATING UPPER BOUNDS

The best upper bound λ_R for an energy eigenvalue calculated with the Rayleigh–Ritz method is given by

$$\lambda_R = R[\Psi] = \sum_{i=1}^{N}\sum_{i=1}^{N} c_i c_j \mathbf{H}_{ij}\,, \quad \|\Psi\| = 1$$

if we denote with c_i the coefficients of the approximate normalized eigenfunction of $\mathcal{H}$.

As there are both positive and negative elements of summation a loss of significance is due to addition errors (significant digits *at the end* of the mantissa get lost) and by subtraction errors (significant digits *at the beginning* of the mantissa get lost). While the latter is inevitable, accuracy loss by addition can be avoided (or at least minimized) by using 128 bit arithmetics instead of 64 bit arithmetics, even if the matrix elements were calculated using 64 bit arithmetics.

The inevitable loss in significance caused by subtraction errors can be quantified by calculating the absolute value of the ratio of the largest term of the summation, S_{max}, to the result of summation $R[\Psi]$. Then the number L of significant digits lost is at least the logarithm of this ratio:

$$L \geqslant \log_{10}\left|\frac{S_{max}}{R[\Psi]}\right|.$$

In order to estimate the loss in significancy for large basis sets, L has been calculated for several *fully linked* and *second order linked* basis sets of the structure $(n,n,n,n/n)_{n,n}$. Tables 6 and 7 show the results.

Table 6
Loss of significant digits in calculating expectation values for the energy: *fully linked* basis sets.

n	Dim	$R[\Psi]$	L
1	12	−1.058 686 435 664 81	0.202
2	36	−1.146 163 982 256 01	0.872
3	76	−1.169 605 199 036 09	1.45
4	152	−1.173 816 001 147 76	2.03
5	264	−1.174 403 573 114 74	2.75
6	440	−1.174 469 271 176 95	3.67

Table 7
Loss of significant digits in calculating expectation values for the energy: *second order linked* basis sets.

n	Dim	$R[\Psi]$	L
1	12	−1.058 686 435 664 82	0.202
2	35	−1.146 149 397 807 68	0.846
3	74	−1.169 588 390 734 99	1.664
4	147	−1.173 809 676 411 96	2.384
5	255	−1.174 400 601 788 33	3.300
6	424	−1.174 467 901 227 39	4.620

The extrapolation of these results leads to the conclusion that for calculations with basis sets with a size of more than 1000 functions all integrals have to be calculated with a higher precision than REAL*8 can supply. As the use of REAL*16 arithmetics implies an enormous increase of CPU-time due to the impossibility of vectorization, we had to dispense with calculations in REAL*16.

7.2. LOSS OF SIGNIFICANCE IN CALCULATING VARIANCES

With the definition of the variance

$$F^2 = \langle H^2 \rangle - \langle H \rangle^2$$

it is obvious that a severe loss of significant digits has to be taken into account. A minimization of the variance directly leads to $\langle H^2 \rangle \sim \langle H \rangle^2$. Hence the minimum loss of significant digits L_{min} can be specified as

$$L_{min} = \log_{10} \frac{\langle H^2 \rangle}{F^2} \,. \tag{26}$$

In order to achieve a variance of about 10^{-8} (as an example), $\langle H^2 \rangle$ and $\langle H \rangle^2$ should have at least the first nine decimal digits in common because both expectation values for H_2 are in the range of $(-1.17)^2 \sim 1.37$. At least these nine decimal digits are inevitably lost. Equation (26) yields a lower bound for the loss in significance. Furthermore it has to be taken into account that digits are lost in calculating the expectation values $\langle H^2 \rangle$ and $\langle H \rangle^2$. They can be analysed as described for the case of upper bound calculations. For several *second order linked* basis sets of the structure $(n, n, n, n/n)_{n,n}$ the results are shown in table 8 and fig. 1.

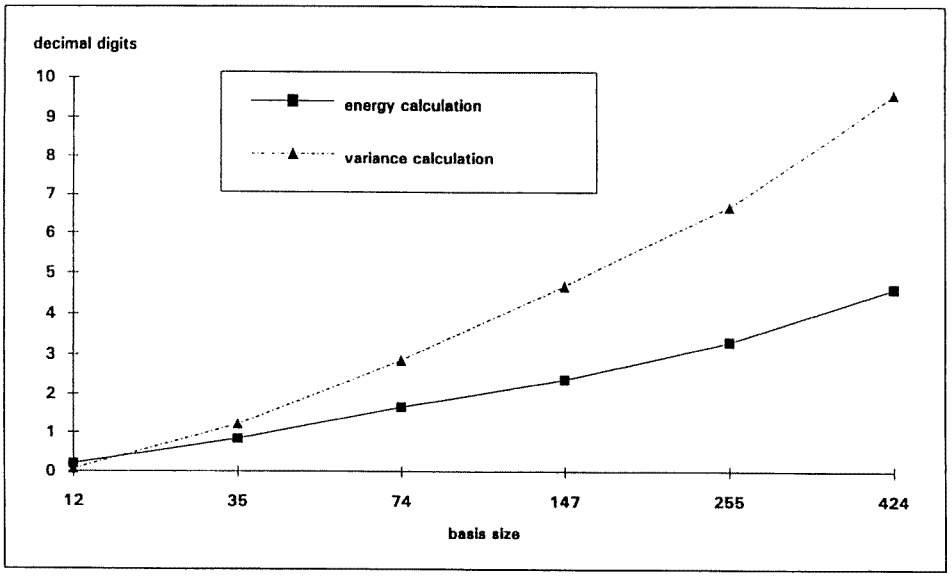

Fig. 1. Loss of significance as function of the basis size.

Table 8
Loss of significant digits in calculating expectation values for the variance: *second order linked* basis sets.

n	Dim	$R[\Psi]$	L
1	12	2.630 153 726 789 61E-1	0.073
2	35	1.510 821 155 888 62E-1	1.218
3	74	4.372 511 757 471 50E-2	2.873
4	147	9.381 090 363 740 53E-3	4.685
5	255	1.520 450 224 130 51E-3	6.685
6	424	2.020 075 947 345 43E-4	9.587

Appendix

A. Auxiliary integrals for upper bound calculations

For the integral

$$V_{11}(m,n) = \int_0^R \int_0^{r_2} r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \tag{27}$$

with

$$m \geqslant 0\,, \quad n \geqslant 0\,,$$

integration by parts with respect to r_1 leads to a stable recursion:

$$V_{11}(m,n) = \frac{1}{m+1}\left(\int_0^R r_2^{m+n+1} e^{-4\alpha r_2}\, dr_2 + 2\alpha V_{11}(m+1,n)\right). \tag{28}$$

Initial values and single integrals are determined numerically with the CADRE subroutine [22].

The auxiliary integral

$$V_{13}(m,n) = \int_0^R \int_R^{\infty} r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \tag{29}$$

factorizes into single integrals which are solved with the CADRE subroutine because no stable analytic solutions can be given for $n<0$.

Solving the auxiliary integral V_{16},

$$V_{16}(m,n) = \int_R^{\infty} \int_{r_2}^{\infty} r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2\,, \tag{30}$$

three cases have to be distinguished:

1. $m \geqslant 0, n \geqslant 0$

With [25]

$$\int_u^\infty x^n e^{-ax}\,dx = e^{-au}\sum_{k=0}^{n}\frac{n!}{k!}\frac{u^k}{a^{n-k+1}}\,, \tag{31}$$

we get the analytic solution

$$V_{16}(m,n) = \frac{m!}{(2\alpha)^{m+n+2}}\frac{e^{-4\alpha R}}{2^{n+1}}\sum_{k=0}^{m}\frac{(n+k)!}{k!2^k}\sum_{l=0}^{n+k}\frac{R^l(4\alpha)^l}{l!}\,. \tag{32}$$

2. $m<0$ and $m+n+1\geqslant 0$

With the substitution $r_1 = xr_2, dr_1 = r_2 dx$, eq. (30) leads to

$$V_{16}(m,n) = \int_R^\infty\int_1^\infty x^m r_2^{m+n+1} e^{-2\alpha(1+x)r_2}\,dx dr_2\,. \tag{33}$$

Changing the sequence of integration and integrating according to (31) with respect to r_2 results in

$$V_{16}(m,n) = \sum_{k=0}^{m+n+1}\frac{(m+n+1)!}{k!}\frac{R^k}{(2\alpha)^{m+n+2-k}}e^{-2\alpha R} \times\int_1^\infty\frac{x^m}{(1+x)^{m+n+2-k}}e^{-2\alpha Rx}\,dx\,. \tag{34}$$

The remaining single integrals are solved numerically.

3. $m<0$ and $m+n+1<0$

Integration by parts with respect to r_1 leads to a stable recursion:

$$V_{16}(m,n) = \frac{1}{m+1}\left(2\alpha V_{16}(m+1,n) - \int_R^\infty r_2^{m+n+1}e^{-2\alpha r_2}\,dr_2\right) \tag{35}$$

with the initial values and single integrals determined numerically.

B. Auxiliary integrals for error interval calculations

B.1. AUXILIARY INTEGRALS FOR THE INTEGRAL I_2

Designating the auxiliary integrals according to the order of appearance with $V_{21},\ldots,V_{28}$, it can be stated:

- The integrals V_{25} to V_{28} can be solved analogously to the integrals in part A.
- The integrals V_{22} and V_{23} are identical as can be shown by changing the order of integration.

1) The integral V_{21}

$$V_{21}(m,n) = \int_0^R \int_0^R \ln \left| \frac{r_1 + r_2}{r_1 - r_2} \right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \tag{36}$$

can be solved by substituting

$$r_1 = tR, \quad r_2 = \tau R,$$

and then

$$\frac{t-\tau}{t+\tau} = x, \quad dt = \frac{-2\tau}{(1-x)^2} dx, \quad t = \frac{1+x}{1-x}\tau,$$

resulting in

$$\begin{aligned} V_{21}(m,n) = &-2R^{m+n+2} \left\{ \int_{-1}^0 \int_0^1 \ln|x| \frac{(1+x)^m}{(1-x)^{m+2}} \tau^{m+n+1} e^{-\frac{4\alpha R}{1-x}\tau}\, d\tau dx \right. \\ &\left. + \int_0^1 \int_0^{\frac{1-x}{1+x}} \ln|x| \frac{(1+x)^m}{(1-x)^{m+2}} \tau^{m+n+1} e^{-\frac{4\alpha R}{1-x}\tau}\, d\tau dx \right\} \\ = &-2R^{m+n+2} \{ V_{211}(m,n) + V_{212}(m,n) \} \end{aligned} \tag{37}$$

with $m + n + 1 \geqslant 0$.

Repetitive integration by parts with respect to τ in V_{211} leads to

$$V_{211}(m,n) = \sum_{k=0}^{\infty} (4\alpha R)^k \prod_{p=0}^{k} \frac{1}{m+n+p+2} \int_{-1}^0 \ln|x| \frac{(1+x)^m}{(1-x)^{m+k+2}} e^{-\frac{4\alpha R}{1-x}}\, dx. \tag{38}$$

In analogy we get for V_{212}

$$V_{212}(m,n) = \sum_{k=0}^{\infty} (4\alpha R)^k \prod_{p=0}^{k} \frac{1}{m+n+p+2} \int_0^1 \ln|x| \frac{(1-x)^n}{(1+x)^{n+k+2}} e^{-\frac{4\alpha R}{1+x}}\, dx, \tag{39}$$

and for $V_{21}(m,n)$

$$\begin{aligned} V_{21}(m,n) = &-2R^{m+n+2} \sum_{k=0}^{\infty} (4\alpha R)^k \prod_{p=0}^{k} \frac{1}{m+n+p+2} \\ &\times \left\{ \int_0^1 \ln|x| \frac{(1-x)^m}{(1+x)^{m+k+2}} e^{-\frac{4\alpha R}{1+x}}\, dx \right. \\ &\left. + \int_0^1 \ln|x| \frac{(1-x)^n}{(1+x)^{n+k+2}} e^{-\frac{4\alpha R}{1+x}}\, dx \right\}. \end{aligned} \tag{40}$$

The remaining single integrals are determined numerically.

2) The integral

$$V_{22}(m,n) = \int_0^R \int_R^\infty \ln\left|\frac{r_1+r_2}{r_1-r_2}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \tag{41}$$

can be transformed into a stable recursion by substituting

(a) $r_1 = tR\,, \quad r_2 = \tau R\,,$

(b) $t = x\tau\,, \quad dt = \tau dx\,, \quad x = t/\tau\,,$

changing the order of integration, and integrating by parts with respect to τ, we receive

$$\begin{aligned} V_{22}(m,n) = &\frac{R^{m+n+2}}{m+n+2}\left\{\int_1^\infty \ln\left|\frac{1+x}{1-x}\right| x^m e^{-2\alpha R(1+x)}\, dx\right. \\ &- \int_1^\infty \ln\left|\frac{1+x}{1-x}\right| x^{-n-2} e^{-2\alpha R(1+\frac{1}{x})}\, dx \\ &\left. + \frac{2\alpha R}{R^{m+n+3}}\left(V_{22}(m,n+1) + V_{22}(m+1,n)\right)\right\}. \end{aligned} \tag{42}$$

Initial values and single integrals are determined numerically.

3) The integral $V_{24}(m,n)$ can be solved using a similar routine as had been established for the solution of V_{22}.

Performing the same substitutions we obtain

$$V_{24}(m,n) = \int_R^\infty \int_R^\infty \ln\left|\frac{r_1+r_2}{r_1-r_2}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \tag{43}$$

$$= R^{m+n+2} \int_1^\infty \int_{\frac{1}{\tau}}^\infty \ln\left|\frac{1+x}{1-x}\right| x^m \tau^{m+n+1} e^{-2\alpha R(1+x)\tau}\, dx d\tau \tag{44}$$

and after interchanging the sequence of integration

$$V_{24}(m,n) = R^{m+n+2}\left(V_{241}(m,n) + V_{242}(m,n)\right) \tag{45}$$

with

$$V_{241}(m,n) = R^{m+n+2} \int_1^\infty \int_1^\infty \ln\left|\frac{1+x}{1-x}\right| x^m \tau^{m+n+1} e^{-2\alpha R(1+x)\tau}\, dx d\tau\,, \tag{46}$$

$$V_{242}(m,n) = R^{m+n+2} \int_0^1 \int_{1/x}^\infty \ln\left|\frac{1+x}{1-x}\right| x^m \tau^{m+n+1} e^{-2\alpha R(1+x)\tau}\, dx d\tau\,. \tag{47}$$

In the case of $m+n+1 \geqslant 0$, these double integrals can be reduced to single integrals using eq. (31). This leads to

$$V_{241}(m,n) = \frac{R^{m+n+2}}{(2\alpha R)^{m+n+2}} \sum_{k=0}^{m+n+1} \frac{(m+n+1)!}{k!} \times (2\alpha R)^k \int_1^\infty \ln\left|\frac{1+x}{1-x}\right| \frac{x^m}{(1+x)^{m+n+2-k}} e^{-2\alpha R(1+x)}\, dx \tag{48}$$

and

$$V_{242}(m,n) = \frac{R^{m+n+2}}{(2\alpha R)^{m+n+2}} \sum_{k=0}^{m+n+1} \frac{(m+n+1)!}{k!} \times (2\alpha R)^k \int_0^1 \ln\left|\frac{1+x}{1-x}\right| \frac{x^{m-k}}{(1+x)^{m+n+2-k}} e^{-2\alpha R(1+\frac{1}{x})}\, dx. \tag{49}$$

Combining both,

$$V_{24}(m,n) = \frac{1}{(2\alpha)^{m+n+2}} \sum_{k=0}^{m+n+1} \frac{(m+n+1)!}{k!} (2\alpha R)^k \times \left(\int_0^1 \ln\left|\frac{1+x}{1-x}\right| \frac{x^{n-k}}{(1+x)^{m+n+2-k}} e^{-2\alpha R(1+\frac{1}{x})}\, dx + \int_0^1 \ln\left|\frac{1+x}{1-x}\right| \frac{x^{m-k}}{(1+x)^{m+n+2-k}} e^{-2\alpha R(1+\frac{1}{x})}\, dx \right). \tag{50}$$

Therefore only one type of single integrals has to be calculated numerically. In the case of $m+n+1<0$ a double recursion can be developed. Integrating both V_{241} and V_{242} by parts with respect to τ and combining the results:

$$V_{24}(m,n) = \frac{R^{m+n+2}}{m+n+2} \left\{ \frac{2\alpha}{R^{m+n+2}} (V_{24}(m,n+1) + V_{24}(m+1,n)) - \int_0^1 \ln\left|\frac{1+x}{1-x}\right| x^{-m-2} e^{-2\alpha R(1+\frac{1}{x})}\, dx - \int_0^1 \ln\left|\frac{1+x}{1-x}\right| x^{-n-2} e^{-2\alpha R(1+\frac{1}{x})}\, dx \right\}. \tag{51}$$

Due to the symmetry of the integrals, only $V_{24}(m_{max}, n)$ are needed as starting values but the singularity $m = -n-2$ demands the calculation of $V_{24}(-n-2, n)$ for all n as well.

B.2. AUXILIARY INTEGRALS FOR THE INTEGRAL I_3

1) Let $V_{31}(m,n)$ be the integral

$$V_{31}(m,n) = \int_R^\infty \int_0^{r_2} \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 . \tag{52}$$

Changing the sequence of integration and integrating with respect to r_2 yields for $n \geqslant 0$

$$\begin{aligned} V_{31}(m,n) = &\sum_{k=0}^{n} \frac{n!}{k!} \frac{1}{(2\alpha)^{n+1-k}} \\ &\times \left(R^k e^{-2\alpha R} \int_0^R \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m e^{-2\alpha r_1}\, dr_1 \right. \\ &\left. + \int_R^\infty \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^{m+k} e^{-4\alpha r_1}\, dr_1 \right) . \end{aligned} \tag{53}$$

In case of $n<0$ integrating by parts with respect to r_2 leads to the recursion

$$\begin{aligned} V_{31}(m,n) = &\frac{1}{n+1} \left\{ 2\alpha V_{31}(m,n+1) - R^{n+1} e^{-2\alpha R} \int_0^R \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m e^{-2\alpha r_1}\, dr_1 \right. \\ &\left. - \int_R^\infty \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^{m+n+1} e^{-4\alpha r_1}\, dr_1 \right\} . \end{aligned} \tag{54}$$

The single integrals and the necessary starting values $V_{31}(m, n_{max})$ (for all m) have to be calculated numerically.

2) The integral

$$V_{32}(m,n) = \int_R^\infty \int_{r_2}^\infty \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \tag{55}$$

can be reduced to single integrals by interchanging the sequence of integration and integrating with respect to r_2:

$$\begin{aligned} V_{32}(m,n) = &\sum_{k=0}^{n} \frac{n!}{k!} \frac{1}{(2\alpha)^{n+1-k}} \\ &\times \left\{ R^k e^{-2\alpha R} \int_R^\infty \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m e^{-2\alpha r_1}\, dr_1 \right. \\ &\left. - \int_R^\infty \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^{m+k+1} e^{-4\alpha r_1}\, dr_1 \right\} . \end{aligned} \tag{56}$$

In case of $m<0$ this solution causes numerical instabilities due to the subtraction procedure. In this case, the recursion

$$V_{32}(m,n)=\frac{1}{n+1}\left\{\int_R^\infty \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^{m+n+1}e^{-4\alpha r_1}\,dr_1 - R^{n+1}e^{-2\alpha R}\int_R^\infty \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m e^{-2\alpha r_1}\,dr_1 + 2\alpha V_{32}(m,n+1)\right\} \quad (57)$$

can be used.

3) For the integral

$$V_{33}(m,n)=\int_0^R\int_0^{r_2}\ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\,dr_1dr_2\,, \quad (58)$$

the preceding routine cannot be applied. In this case only the recursion

$$V_{33}(m,n)=\frac{1}{n+1}\left\{R^{n+1}e^{-2\alpha R}\int_0^R \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m e^{-2\alpha r_1}\,dr_1 - \int_0^R \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^{m+n+1}e^{-2\alpha r_1}\,dr_1 + 2\alpha V_{33}(m,n+1)\right\} \quad (59)$$

can be applied, because integration with respect to r_2 leads to numerical instabilities due to subtraction errors.

4) The integral V_{34}

$$V_{34}(m,n)=\int_0^R\int_{r_2}^\infty\ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\,dr_1dr_2 \quad (60)$$

decomposes into two terms after interchanging the sequence of integration:

$$V_{34}(m,n)=V_{341}(m,n)+V_{342}(m,n)$$

with

$$V_{341}(m,n)=\int_0^R\int_0^{r_1}\ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\,dr_1dr_2 \quad (61)$$

and

$$V_{342}(m,n)=\int_0^R r_2^n e^{-2\alpha r_2}\,dr_2\int_R^\infty\ln\left|\frac{r_1+R}{r_1-R}\right| r_1^m e^{-2\alpha r_1}\,dr_1\,. \quad (62)$$

V_{342} factorizes, while for V_{341} a stable recursion can be derived:

$$V_{341}(m,n) = \frac{1}{n+1}\left\{\int_0^R \ln\left|\frac{r_1+R}{r_1-R}\right| r_1^{m+n+1} e^{-4\alpha r_1}\, dr_1 + 2\alpha V_{341}(m,n+1)\right\} \tag{63}$$

with $m+n+1 \geqslant 0$.

5) Similarly the integral $V_{35}(m,n)$ decomposes into two terms, one of which (V_{351}) factorizes, while the other can be solved analytically for $n \geqslant 0$ and recursively for $n<0$:

$$V_{35}(m,n) = \int_R^\infty \int_0^{r_2} r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \tag{64}$$

$$= \int_0^R \int_R^\infty r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_2 dr_1 + \int_R^\infty \int_{r_2}^\infty r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_2 dr_1$$

$$= V_{351}(m,n) + V_{352}(m,n)\,. \tag{65}$$

Solving the integral V_{352} two cases have to be distinguished:

(a) $n \geqslant 0$. Using eq. (31) leads to the analytical solution

$$V_{352}(m,n) = \frac{n!e^{-4\alpha R}}{(2\alpha)^{m+n+2}2^{m+1}} \sum_{k=0}^{n} \frac{(m+k)!}{2^k k!} \sum_{l=0}^{m+k} \frac{(4\alpha R)^l}{l!}\,. \tag{66}$$

(b) $n<0$. Integration by parts with respect to r_2 leads to an instable recursion for V_{352}. A stable recursion can be derived by integrating V_{35} by parts with respect to r_1:

$$V_{35}(m,n) = \frac{1}{m+1}\left\{2\alpha V_{35}(m,n+1) + \int_R^\infty r_2^{m+n+1} e^{-4\alpha r_2}\, dr_2\right\}. \tag{67}$$

6) The integrals V_{36} and V_{37} are identical with V_{16} and V_{11}.

7) The integral

$$V_{38}(m,n) = \int_0^R \int_{r_2}^\infty r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \tag{68}$$

can be reduced to a sum of single integrals for $m \geqslant 0$:

$$V_{38}(m,n) = \frac{m!}{(2\alpha)^{m+1}} \sum_{k=0}^{m} \frac{(2\alpha)^k}{k!} \int_0^R r_2^{n+k} e^{-4\alpha r_2}\, dr_2\,. \tag{69}$$

If $m<0$, integration by parts with respect to r_1 leads to a stable recursion:

$$V_{38}(m,n) = \frac{1}{m+1}\left\{2\alpha V_{38}(m+1,n) - \int_0^R r_2^{m+n+1} e^{-4\alpha r_2}\, dr_2\right\}. \tag{70}$$

Computing the starting values it proved to be profitable to perform the numerical integrations on the following integral, which can be derived by substituting $r_1 = xr_2$:

$$V_{38}(m,n) = \int_0^R \int_1^\infty x^m r_2^{m+n+1} e^{-2\alpha(1+x)r_2}\, dx dr_2 \tag{71}$$

$$= \int_0^R \int_0^1 x^{-m-2} r_2^{m+n+1} e^{-2\alpha(1+\frac{1}{x})r_2}\, dx dr_2\,. \tag{72}$$

Otherwise, the domain of integration would be too large, which causes serious convergence problems.

B.3. AUXILIARY INTEGRALS FOR THE INTEGRAL I_{41}

Let the double integrals be denoted with V_{41} and V_{42} according to their order of appearance.

Thus the former integral can be solved recursively after applying the already familiar techniques – substituting $r_1 = xr_2$, interchanging the sequence of integration and integrating by parts with respect to r_2:

$$V_{41}(m,n) = \int_0^\infty \int_0^\epsilon \ln\left|\frac{r_1+r_2}{r_1-r_2}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_2 dr_1$$

$$= \int_0^\epsilon \int_0^\infty \ln\left|\frac{r_1+r_2}{r_1-r_2}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_1 dr_2 \tag{73}$$

$$= \int_0^\epsilon \int_0^\infty \ln\left|\frac{1+x}{1-x}\right| x^m r_2^{m+n+1} e^{-2\alpha(1+x)r_2}\, dx dr_2 \tag{74}$$

$$= \int_0^\infty \ln\left|\frac{1+x}{1-x}\right| x^m \int_0^\epsilon r_2^{m+n+1} e^{-2\alpha(1+x)r_2}\, dr_2\, dx \tag{75}$$

$$= \frac{1}{m+n+2}\left[\epsilon^{m+n+2} e^{-2\alpha\epsilon} \int_0^\infty \ln\left|\frac{1+x}{1-x}\right| x^m e^{-2\alpha\epsilon x}\, dx \right.$$

$$\left. + 2\alpha\epsilon(V_{41}(m+1,n) + V_{41}(m,n+1))\right] \tag{76}$$

with $m>0$, and $n>0$.

At this point the reason for the restriction of the parameter ϵ can be understood. The domain of the single integral in eq. (77) stretches from 0 to ∞. The integral is finite, as the powers of x are compensated by the exponential-function. Now the smaller we choose ϵ the worse is the convergence of the exponential function. For

constant x the functional value increases for decreasing values of ϵ. This is a crucial point in the numerical computation of the integrals, because functional values have to be calculated explicitly. Increase beyond the largest internally producible number (REAL*8: $z_{max} \sim 10^{309}$), yields a run time error and the integral cannot be computed.

The second double integral factorizes:

$$V_{42}(m,n) = \int_0^\infty \int_0^\epsilon r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_2 dr_1 \tag{77}$$

$$= \frac{m!}{(2\alpha)^{m+1}} \int_0^\epsilon r_2^n e^{-2\alpha r_2} dr_2 \tag{78}$$

with $m > 0$, and $n > 0$.

B.4. AUXILIARY INTEGRALS FOR THE INTEGRAL I_{42}

Let the double integrals be denoted as V_{51} to V_{54}.

The integral V_{51} can neither be solved analytically nor by recursion, because due to the logarithmic terms integration by parts induces new types of integrals. As only a few integrals of this type are necessary (about 2000), they are computated numerically. An efficient numerical computation requires several substitutions as well as intersections of the domain of integration:

$$V_{51}(m,n) = \int_0^\infty \int_\epsilon^\infty \ln\left|\frac{r_1+r_2}{r_1-r_2}\right| \ln\left|\frac{r_2+R}{r_2-R}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_2 dr_1 \tag{79}$$

$$= \int_0^\infty \int_\epsilon^\infty \ln\left|\frac{1+x}{1-x}\right| \ln\left|\frac{r_2+R}{r_2-R}\right| x^m r_2^{m+n+1} e^{-2\alpha(1+x)r_2}\, dr_2 dx \tag{80}$$

$$V_{51}(m,n) = \int_0^\infty \int_\epsilon^\infty \ln\left|\frac{1+x}{1-x}\right| \ln\left|\frac{y+R}{y-R}\right| x^m y^{m+n+1} e^{-2\alpha(1+x)y}\, dy dx \tag{81}$$

$$= \int_0^1 \int_\epsilon^\infty \ln\left|\frac{1+x}{1-x}\right| \ln\left|\frac{y+R}{y-R}\right| x^m y^{m+n+1} e^{-2\alpha(1+x)y}\, dy dx$$

$$+ \int_0^1 \int_\epsilon^\infty \ln\left|\frac{1+x}{1-x}\right| \ln\left|\frac{y+R}{y-R}\right| \frac{1}{x^{m+2}} y^{m+n+1} e^{-2\alpha(1+\frac{1}{x})y}\, dy dx \tag{82}$$

$$= \int_0^1 \int_\epsilon^R \ln\left|\frac{1+x}{1-x}\right| \ln\left|\frac{y+R}{y-R}\right| x^m y^{m+n+1} e^{-2\alpha(1+x)y}\, dy dx$$

$$+\int_0^1\int_\epsilon^R \ln\left|\frac{1+x}{1-x}\right| \ln\left|\frac{y+R}{y-R}\right| \frac{1}{x^{m+2}} y^{m+n+1} e^{-2\alpha(1+\frac{1}{x})y}\, dydx$$

$$+\int_0^1\int_0^{\frac{1}{R}} \ln\left|\frac{1+x}{1-x}\right| \ln\left|\frac{\frac{1}{y}+R}{\frac{1}{y}-R}\right| x^m \frac{1}{y^{m+n+3}} e^{-2\alpha(1+x)/y}\, dydx$$

$$+\int_0^1\int_0^{\frac{1}{R}} \ln\left|\frac{1+x}{1-x}\right| \ln\left|\frac{\frac{1}{y}+R}{\frac{1}{y}-R}\right| \frac{1}{x^{m+2}} \frac{1}{y^{m+n+3}} e^{-2\alpha(1+\frac{1}{x})/y}\, dydx\,. \tag{83}$$

For the integral V_{53} substituting $r_1 = xr_2$ and interchanging the sequence of integration leads to the recursion

$$V_{53}(m,n) = \int_0^\infty\int_\epsilon^\infty \ln\left|\frac{r_1+r_2}{r_1-r_2}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_2dr_1 \tag{84}$$

$$= \int_0^\infty\int_\epsilon^\infty \ln\left|\frac{1+x}{1-x}\right| x^m r_2^{m+n+1} e^{-2\alpha(1+x)r_2}\, dr_2dx \tag{85}$$

$$= \frac{1}{m+n+2}\left[2\alpha(V_{53}(m,n+1)+V_{53}(m+1,n))\right.$$

$$\left. - \epsilon^{m+n+2} e^{-2\alpha\epsilon} \int_0^\infty \ln\left|\frac{1+x}{1-x}\right| x^m e^{-2\alpha\epsilon x}\, dx\right] \tag{86}$$

with

$$m+n+2>0\,.$$

The integrals V_{52} and V_{54} factorize:

$$V_{52}(m,n) = \int_0^\infty\int_\epsilon^\infty \ln\left|\frac{r_2+R}{r_2-R}\right| r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_2dr_1 \tag{87}$$

$$= \frac{m!}{(2\alpha)^{m+1}} \int_\epsilon^\infty \ln\left|\frac{r_2+R}{r_2-R}\right| r_2^n e^{-2\alpha r_2}\, dr_2 \tag{88}$$

with $m>0$ and $n>0$;

$$V_{54}(m,n) = \int_0^\infty\int_\epsilon^\infty r_1^m r_2^n e^{-2\alpha(r_1+r_2)}\, dr_2dr_1 \tag{89}$$

$$= \frac{m!}{(2\alpha)^{m+1}} \int_\epsilon^\infty r_2^n e^{-2\alpha r_2}\, dr_2 \tag{90}$$

with $m>0$, and $n>0$.

References

[1] W. Heitler and F. London, Z. Phys. 44 (1927) 455.
[2] H.M. James and A.S. Coolidge, J. Chem. Phys. 1 (1933) 825.

[3] D.M. Bishop and L.M. Cheung, Phys. Rev. A18 (1978) 61846.
[4] W. Kolos, K. Szalewicz and H.J. Monkhorst, J. Chem. Phys. 84 (1986) 3278.
[5] H. Beutler, Z. Phys. Chem. B29 (1935) 315.
[6] G. Herzberg and A. Monfils, J. Mol. Spectr. 5 (1960) 482.
[7] G. Herzberg, J. Mol. Spectr. 33 (1970) 147.
[8] E. McCormack and E.E. Eyler, Bull. Am. Phys. Soc. 32 (1987) 1279.
[9] H. Kleindienst and R. Emrich, *Int. Series of Numerical Mathematics*, Vol. 96 (Birkhäuser, Basel, 1991) pp. 131–142.
[10] H. Kleindienst, *Untersuchungen über das Spektrum von Schrödinger-Operatoren* (Habilitationsschrift, Düsseldorf, 1975).
[11] H. Kleindienst and W. Altmann, Int. J. Quant. Chem. 10 (1976) 873.
[12] H. Kleindienst and W. Müller, Theoret. Chim. Acta (Berl.) 56 (1980) 183.
[13] H. Kleindienst and D. Hoppe, Theor. Chim. Acta 70 (1986) 221.
[14] H. Kleindienst and A. Müller, Chem. Phys. Lett. 157 (1989) 426.
[15] G. Temple, Proc. R. Soc. London Ser. A119 (1928) 276.
[16] E.O. Steinborn and E. Filter, Theor. Chim. Acta (Berl.) 38 (1975) 261.
[17] A. Lüchow and H. Kleindienst, Int. J. Quant. Chem. 41 (1992) 719.
[18] L. Wolniewicz, Acta Phys. Polon. 22 (suppl.) (1962) 3.
[19] A.A. Frost, Theor. Chim. Acta (Berl.) 1 (1962) 36.
[20] H. Kleindienst and S. Beutner, Chem. Phys. Lett. 164 (1989) 291.
[21] J.F. Perkins, J. Chem. Phys. 48 (1968) 1985.
[22] C. de Boor, in: J.R. Rice (Hrsg.), Mathematical Software (New York, 1971) S. 417.
[23] D. Levin, Int. J. Comp. Math. B3 (1973) 371.
[24] A. Lüchow, H. Kleindienst, Comp. Chem. 17 (1993) 61.
[25] I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products*, Corrected and Enlarged Ed. (Academic Press, New York, 1988).