Numerical Calculation of Adiabatic Corrections with the Born-Handy Method[*]

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Abstract: A modified algorithm of the numerical calculation of adiabatic corrections is proposed. It is based on earlier approaches, introduced by Cencek and Kutzelnigg and by the present author. The adiabatic correction is approximated in terms of overlap integrals between electronic wave functions for a given geometry and for a single nucleus shifted by h. The leading term of error is proportional to the square of h in the original methods. The new approach, while requires the same wave functions as those methods, shrinks the error, so that it becomes proportional to h^4 in atomic cases. Test calculations show, that similar behavior is retained also for two–atom molecules and additional stable decimal digit of the adiabatic correction can be obtained.

Key words: adiabatic correction, explicitly correlated Gaussian function, Born-Handy method

I. INTRODUCTION

The separation of nuclear motions within the adiabatic approximation is a foundation of almost all quantum chemical calculations. Following the textbooks of quantum chemistry, the wave function is assumed in the form of a product of functions describing the nuclei (which coordinates will be denoted by **R**) and light particles (with coordinates denoted by **r**):

$$\Psi(\mathbf{R},\mathbf{r}) = \Psi_n(\mathbf{R})\,\Psi_l(\mathbf{R},\mathbf{r}). \qquad (1)$$

The function Ψ_l is usually called as the electronic function, but it is also obvious to treat the positrons on equal footing with electrons, as their masses are the same and they often move in the same time scale. As both electrons and positrons are leptons and wave functions for positronic atoms and molecules will be used in calculations presented in this article, Ψ_l will be named as the leptonic function.

The nuclear kinetic energy operator $\left(\hat{T}_n\right)$ is separated out of the hamiltonian

$$\hat{H}(\mathbf{R},\mathbf{r}) = \hat{T}_n(\mathbf{R}) + \hat{H}_l(\mathbf{R},\mathbf{r}) \qquad (2)$$

and the Schrödinger equation for the leptonic wave function (with the leptonic hamiltonian $\hat{H}_l$) is solved for various, fixed positions of the nuclei, giving the leptonic (or electronic) energy, E_l dependent on **R**

$$\hat{H}_l\Psi_l(\mathbf{R},\mathbf{r}) = E_l(\mathbf{R})\Psi_l(\mathbf{R},\mathbf{r}), \qquad (3)$$

and providing the potential energy for nuclear function, which can be obtained by solving of the following equation:

$$\left[\hat{T}_n(\mathbf{R}) + E_l(\mathbf{R}) + E_{ad}(\mathbf{R})\right]\Psi_n(\mathbf{R}) = E\,\Psi_n(\mathbf{R}). \qquad (4)$$

The adiabatic correction is expectation value of the $\hat{T}_n$ operator

$$E_{ad}(\mathbf{R}) = \left\langle \Psi_l(\mathbf{R},\mathbf{r}) \middle| \hat{T}_n(\mathbf{R}) \middle| \Psi_l(\mathbf{R},\mathbf{r}) \right\rangle \qquad (5)$$

and measures the changes of leptonic wave function, induced by moving the nuclei from their current positions. It is not trivial to calculate E_{ad} for all but atomic systems and it is usually neglected within the Born-Oppenheimer approximation. This is justified, as the values of adiabatic correction are usually much smaller than these of leptonic energies. In most calculations, carried out in practice, they are even within the error margins of E_l, as the accuracy of solutions of equation (3) is too low. However, the recent progress in development of computational methods, achieved in the group of professor Rychlewski, made it possible to obtain electronic energies having spectroscopic accuracy (i.e. with the error not exceeding a few microhartrees) for

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[*]This article is dedicated to the memory of Professor Jacek Rychlewski

3- and 4-electron molecules (see [1] for a review). If the results of theoretical studies are to be compared with precise experimental measurements, the adiabatic correction can no longer be omitted.

The traditional way of calculation of E_{ad} requires explicit separation of center of mass coordinates, which becomes very complicated beyond 2 nuclei [2]. Internal coordinates, mixing electronic and nuclear degrees of freedom, are introduced by that procedure. On the other hand, a pragmatic method has been proposed, in which the adiabatic correction is computed directly in the laboratory coordinate frame [3, 4]. The equivalence of both approaches has been proven by Kutzelnigg [5]. The latter approach of calculation of E_{ad} has been named as the Born-Handy method. It provides a general framework, which can be applied for molecules of any geometry and was already used in practice with higly accurate explictly correlated Gaussian (ECG) wave functions [6]. It will be briefly discussed in the next section. Atomic units are used in the whole text.

II. METHOD

As no internal coordinates are introduced in the Born--Handy method, the adiabatic correction can be written as the sum of atomic contributions:

$$E_{ad} = \sum_{A=1}^{N_{nuc}} -\frac{1}{2M_A}\Delta_A, \qquad (6)$$

where Δ_A are the expectation values of ∇^2 operators, related to the coordinates of respective nuclei. It should be pointed out, that such a (formal) partitioning is related only to the concrete procedure, which is used in the present work and has nothing to do with a physical interpretation of the components of E_{ad}. In the cartesian coordinate frame, which is most convenient for calculations with ECG functions, each Δ_A integral is the following sum:

$$\Delta_A = \Delta_{x,A} + \Delta_{y,A} + \Delta_{z,A} =$$

$$= \left\langle \Psi_l \left| \frac{\partial^2}{\partial x_A^2} \right| \Psi_l \right\rangle + \left\langle \Psi_l \left| \frac{\partial^2}{\partial y_A^2} \right| \Psi_l \right\rangle + \left\langle \Psi_l \left| \frac{\partial^2}{\partial z_A^2} \right| \Psi_l \right\rangle. \qquad (7)$$

The integrals $\Delta_{x,A}, \Delta_{y,A}$ and $\Delta_{z,A}$ are dependent on the rotation of coordinate frame, while Δ_A is invariant.

Two similar algorithms, based on the numerical approximations of derivatives of the wave function (discussed in many textbooks of numerical methods),

$$\frac{\partial \Psi_l(Q)}{\partial Q} \approx \frac{\Psi_l(Q+h) + \Psi_l(Q-h)}{2h} \qquad (8)$$

and

$$\frac{\partial^2 \Psi_l(Q)}{\partial Q^2} \approx \frac{\Psi_l(Q+h) + \Psi_l(Q-h) - 2\Psi_l(Q)}{h^2}, \qquad (9)$$

have been developed and applied in the calculations of E_{ad} with ECG functions. The symbol Q in Eqs. (8) and (9) denotes the x, y or z coordinate of a chosen nucleus. The respective expectation value of operator of 2'nd derivative will be denoted as

$$\Delta_Q = \left\langle \Psi_l \left| \frac{\partial^2 \Psi_l(Q)}{\partial Q^2} \right. \right\rangle. \qquad (10)$$

The differentiation of normalization condition of the electronic wave function over Q leads to another well known relation

$$\left\langle \Psi_l \left| \frac{\partial^2 \Psi_l(Q)}{\partial Q^2} \right. \right\rangle = -\left\langle \frac{\partial \Psi_l(Q)}{\partial Q} \left| \frac{\partial \Psi_l(Q)}{\partial Q} \right. \right\rangle. \qquad (11)$$

This relation, combined with equation (8) [7], leads to the approximation proposed by Cencek and Kutzelnigg. The integration over coordinates of light particles gives

$$\Delta_Q^{(1)} = \frac{S_\pm - 1}{2h^2}. \qquad (12)$$

This formula is also implemented in the PSI3 quantum chemistry code [8] for the Hartree-Fock and CI wave functions. Multiplication of Eq. (9) by Ψ_l^* and similar integration gives the formula used recently by the present author [9, 10],

$$\Delta_Q^{(2)} = \frac{S_+ + S_- - 2}{h^2}. \qquad (13)$$

Symbols S_+, S_- and $S_\pm$ denote the overlap integrals between leptonic wave functions of the system with a little different geometries, i.e. the chosen coordinate (Q) of a nucleus is shifted by h:

$$S_+ = \left\langle \Psi_l(Q) \middle| \Psi_l(Q+h) \right\rangle, \qquad (14)$$

$$S_- = \left\langle \Psi_l(Q) \middle| \Psi_l(Q-h) \right\rangle, \qquad (15)$$

and

$$S_\pm = \left\langle \Psi_l(Q-h) \middle| \Psi_l(Q+h) \right\rangle. \qquad (16)$$

The leading term of error in approximations (12) and (13) is proportional to h^2. Only one overlap integral is needed for formula (12), while (13) requires two integrals, but their calculation is cheaper than solving the leptonic Schrödinger equation for $Q + h$ and $Q - h$, which is needed in both methods. The goal of present work is construction of an algorithm, which would use the same wave functions (for Q, $Q + h$ and $Q - h$), but with a faster decreasing error.

Let us consider the Δ_Q integral for an isolated atom. Shift of the nucleus results in a translation of the whole wave function, so

$$S_+(h) = S_-(h) = S_\pm\left(\frac{h}{2}\right). \tag{17}$$

Equation (12) becomes equivalent with (13) for halved shift h, giving

$$\Delta_Q^{(1)}\left(\frac{h}{2}\right) = \Delta_Q^{(2)}(h). \tag{18}$$

Therefore, the leading component of error of the approximation $\Delta_Q^{(1)}$ is 4 times larger than that of $\Delta_Q^{(2)}$, for a given h. It can be eliminated in the following expression

$$\Delta_Q^{(3)} = \frac{4\Delta_Q^{(2)} - \Delta_Q^{(1)}}{3} = \frac{8(S_+ + S_-) - S_\pm - 15}{6h^2}. \tag{19}$$

For atoms, the error of approximation (19) decreases as h^4. However, moving a single nucleus in a molecule causes more complicated changes of the structure of wave function of light particles. Application of formula (19) requires then a silent assumption, that equation (17) is approximately fulfilled and the term of error, proportional to h^2, is largely cancelled.

III. TEST CALCULATIONS

In order to check the convergence patterns and final accuracy of Δ_A integrals, test calculations have been carried out for normal and positronic atoms and molecules containing up to 5 light particles. All systems were in their ground states. The results given by well grounded Eqs. (12) and (13) are compared with these of formula (19).

The leptonic wave functions of all systems, besides of the hydrogen atom, were linear combinations of explicitly correlated Gaussian (ECG) functions

$$\Psi_l = \sum_l C_l \hat{A}\hat{P}e^{-\sum_{i=1}^N \alpha_i^{(I)}\left(\mathbf{r}_i - \mathbf{R}_i^{(I)}\right)^2 - \sum_{i>j}^N \beta_{ij}^{(I)}\left(\mathbf{r}_i - \mathbf{r}_j\right)^2} \Theta_{S,M_S}, \tag{20}$$

with optimized nonlinear parameters $\alpha_i^{(I)}$, $\beta_i^{(I)}$ and $\mathbf{R}_i^{(I)}$. Θ_{S,M_S} is the spin function, $\hat{A}$ is the antisymmetrizer, which interchanges indistinguishable particles, while $\hat{P}$ ensures proper spatial symmetry of the wave function.

All calculations have been carried out in double precision. The mantissa of a double precision variable contains 53 bits. The numerical differentiation leads to a loss of accuracy, as numbers having similar values are substracted. In this operation, the leading significant bits are lost. Another source of uncertainty is the numerical noise, resulting from accumulating round-off errors and giving pseudorandom least significant bits in the variable. They

are dependent on the processor type, compiler options etc. In order to estimate the number of certain significant bits (N_{bits}), the overlap integral of leptonic wave function with itself

$$S_0 = \left\langle \Psi_l(Q) \middle| \Psi_l(Q) \right\rangle \tag{21}$$

was computed. Without the noise, it would be equal to one. In reality, its value differs slightly from one, and

$$N_{bits} = \left[-\log_2|1 - S_0|\right] \tag{22}$$

where square brackets denote the integer part of a number.

For each system, the convergence Δ_Q of was studied, by performing calculations with different shifts h, starting from 0.032 and halving it, until $h < 0.00002$. The numbers of stable and lost bits were calculated in each step. The leading bits of results were considered stable, if they did not change in two subsequent steps,

$$\text{stable} = \left[\log_2\left|\frac{\Delta_Q(h)}{\Delta_Q(h) - \Delta_Q(2h)}\right|\right] \tag{23}$$

while the number of lost bits resulted from the substraction of similar numbers and was calculated as

$$\text{loss(1)} = \log_2\frac{1}{1 - S_\pm} \tag{24}$$

for Eq. (12),

$$\text{loss(2)} = \log_2\frac{2}{2 - S_+ - S_-} \tag{25}$$

for Eq. (13) and

$$\text{loss(3)} = \log_2\frac{16}{15 + S_\pm - 8(S_+ + S_-)} \tag{26}$$

for Eq. (19). The sum of numbers of stable and lost bits could not exceed the number of noise-free bits. If it did, then the extra accuracy was assumed to be a coincidence and the number of stable bits was assumed to be the difference between N_{bits} and the number of lost bits. For convenience, the numbers of bits were also transformed to the numbers of decimal digits, using the formula $\text{decimal} = \log_{10}2^{bits}$ (this is the reason of some inaccuracies, as the digits were not counted explicitly, but their number was calculated from the respective number of bits). Both numbers are given in the columns of tables, labeled "stable" and "loss", in the form bits/decimal digits.

III.1. Atoms

The calculations of integrals for atoms were an important part of the present study, as they offer a possibility to check independently the results, using analytical values. $\Delta_{x,A}$, $\Delta_{y,A}$ and $\Delta_{z,A}$ are equal, so that only one integral was com-

Table 1. H, analytical wave function; $E_l = -0.5$, $\Delta_H = -1$, $S_0 = 1$, $N_{\text{bits}} = 53$

h	$-\Delta_H^{(2)}$	stable	error	loss	$-\Delta_H^{(3)}$	stable	error	loss
0.032	0.9997483257		2.517e−04	13/3	0.9999943464		5.654e−06	13/3
0.016	0.9999365434	12/3	6.346e−05	15/4	0.9999992827	17/5	7.174e−07	15/4
0.008	0.9999840681	14/4	1.593e−05	17/5	0.9999999096	20/6	9.036e−08	17/5
0.004	0.9999960085	16/4	3.991e−06	19/5	0.9999999886	23/6	1.135e−08	19/5
0.002	0.9999990011	18/5	9.989e−07	21/6	0.9999999986	26/7	1.410e−09	21/6
0.001	0.9999997503	20/6	2.497e−07	23/6	1.0000000001	29/8	1.400e−10	23/6
0.0005	0.9999999389	22/6	6.114e−08	25/7	1.0000000010	28/8	1.030e−09	25/7
0.00025	0.9999999762	24/7	2.384e−08	27/8	0.9999999833	25/7	1.674e−08	27/8
0.000125	0.9999999975	24/7	2.520e−09	29/8	0.9999999975	24/7	2.520e−09	29/8
6.25e−05	0.9999999975	22/6	2.520e−09	31/9	0.9999998838	22/6	1.162e−07	31/9
3.125e−05	0.9999996564	20/6	3.436e−07	33/9	0.9999994290	20/6	5.710e−07	33/9

Table 2. He, 100 ECG functions; $E_l = -2.903724347$, $\Delta_{\text{He}} = -6.12558815759$, $S_0 = 1.000000000000013$, $N_{\text{bits}} = 46$

h	$-\Delta_{\text{He}}^{(2)}$	stable	error	loss	$-\Delta_{\text{He}}^{(3)}$	stable	error	loss
0.032	6.1186495985		6.939e−03	10/3	6.1253305342		2.576e−04	10/3
0.016	6.1238290151	10/3	1.759e−03	12/3	6.1255554873	14/4	3.267e−05	12/3
0.008	6.1251452889	12/3	4.429e−04	14/4	6.1255840468	17/5	4.111e−06	14/4
0.004	6.1254770485	14/4	1.111e−04	16/4	6.1255876351	20/6	5.225e−07	16/4
0.002	6.1255603261	16/4	2.783e−05	18/5	6.1255880854	23/6	7.215e−08	18/5
0.001	6.1255811057	18/5	7.052e−06	20/6	6.1255880324	26/7	1.252e−07	20/6
0.0005	6.1255863075	20/6	1.850e−06	22/6	6.1255880404	24/7	1.172e−07	22/6
0.00025	6.1255861610	22/6	1.997e−06	24/7	6.1255861112	21/6	2.046e−06	24/7
0.000125	6.1255924067	19/5	4.249e−06	26/7	6.1255944956	19/5	6.338e−06	26/7
6.25e−05	6.1255938135	18/5	5.656e−06	28/8	6.1255943820	18/5	6.224e−06	28/8
3.125e−05	6.1256037043	16/4	1.555e−05	30/9	6.1256068875	16/4	1.873e−05	30/9

Table 3. PsH, 768 ECG functions; $E_l = -0.78919627$, $\Delta_H = -1.19821626758$, $S_0 = 0.9999999999999305$, $N_{\text{bits}} = 43$

h	$-\Delta_H^{(2)}$	stable	error	loss	$-\Delta_H^{(3)}$	stable	error	loss
0.032	1.1979003444		3.159e−04	12/3	1.1982098962		6.371e−06	13/3
0.016	1.1981366847	12/3	7.958e−05	14/4	1.1982154649	17/5	8.027e−07	15/4
0.008	1.1981963053	14/4	1.996e−05	16/4	1.1982161788	20/6	8.882e−08	17/5
0.004	1.1982112657	16/4	5.002e−06	18/5	1.1982162525	23/6	1.503e−08	19/5
0.002	1.1982149994	18/5	1.268e−06	20/6	1.1982162440	22/6	2.358e−08	21/6
0.001	1.1982159045	20/6	3.631e−07	22/6	1.1982162063	20/6	6.132e−08	23/6
0.0005	1.1982159665	19/5	3.011e−07	24/7	1.1982159869	18/5	2.807e−07	25/7
0.00025	1.1982224493	17/5	6.182e−06	26/7	1.1982246093	16/4	8.342e−06	27/8
0.000125	1.1982624812	14/4	4.621e−05	28/8	1.1982758110	14/4	5.954e−05	29/8
6.25e−05	1.1983526065	13/3	1.363e−04	30/9	1.1983827335	12/3	1.665e−04	31/9
3.125e−05	1.1989886843	10/3	7.724e−04	32/9	1.1992005966	10/3	9.843e−04	33/9

puted and multiplied by 3. Only the results obtained with Eq. (13) are given in Table 1-4, due to equality (18).

For the ground state of hydrogen atom, the analytical wave function has been used. The overlap integral was also calculated analytically [11] $\left(S(h) = \left\langle \Psi_l(Q) \middle| \Psi_l(Q+h) \right\rangle = (1+h+h^3/3)e^{-h} \right)$, so that it can be safely assumed, that no numerical noise was present. As can be seen in Table 1, faster convergence of the value of Δ_A is achieved with equation (19). The most accurate result has been obtained for $h = 0.001$, where also the largest number of stable bits has been reached. The error is even smaller than suggested by the number of stable bits. Formula (13) gives the smallest error for $h = 0.000125$, but maximal number of stable bits is reached for $h = 0.00025$. This discrepancy may be a coincidence, but may also appear, because the calculations were carried out on the Intel i486 processor, whose floating point unit registers have the internal precision of 80 bits (with 64 bits of mantissa). Even if the "illegally" more accurate value would be accepted, its error is anyway one order of magnitude larger than that given by Eq. (19).

In all other cases, the wave functions are approximations given by equation (20). The numerical noise causes, that the best accuracy of E_{ad} is lower than for H atom and is reached at larger h. The calculations have been carried out for atoms of helium, positronium hydride and positronic lithium. Expansion lengths, leptonic energies, reference values of Δ_A integrals (calculated analytically), S_0 integrals and numbers of certain significant bits are given in the captions of respective tables. The accuracy of wave functions decreases with the system size, but they can be all considered to be of high quality. The errors of leptonic energies amount to about 10 nanohartrees for He, 0.7 microhartree for PsH and no more than 5 microhartrees for PsLi$^+$ [12]. The energy of the latter system is the lowest

published to date, being about 10 μhartrees below the recent result of Mitroy [13].

The same convergence pattern is repeated for all systems – the values of Δ_A increase to the most accurate one, which is reached at $h = 0.0005$ with formula (13) and at $h = 0.002$ (0.004 for PsH) with formula (19). Further decreasing of displacements causes the loss of accuracy, due to the numerical instability. Formula (19) gives 2-5 more stable bits (1 decimal digit) and error smaller by order of magnitude than (12) and (13). The numbers of bits free of the numerical noise are smaller than 53 and decrease with the number of light particles and expansion length.

III.2. Diatomic systems

The calculations of Δ_A integrals for molecules provided the real test of new algorithm, which is not necessarily correct, as Eq. (17) is not automatically fulfilled. They have been carried out for the hydrogen molecule (with two wave functions of different accuracy), helium dimer and positronic lithium hydride molecule, at equilibrium internuclear distances of 1.4011 bohr for H$_2$, 5.6 bohr for He···He and 3.365 bohr for e$^+$LiH. The wave function of positronic LiH was the least accurate of all systems – the energy error is estimated to be of the order of 0.1 millihartree [12].

No analytical reference results could be obtained for molecular systems. The accuracy of Δ_Q was controlled in two ways. First, the stable bits were counted, similarly as for atoms. The results were also compared with the values provided by extrapolation procedure, which is equivalent with Eq. (19) for atoms:

$$\Delta_Q^{(4)} = \frac{4\Delta_Q^{(1)} - \Delta_Q^{(1)}(2h)}{3}, \tag{27}$$

Table 5. H$_2$, 75 ECG functions; $E_l = -1.1744751$, $S_0 = 0.9999999999999685$, $N_{\text{bits}} = 44$

h	$-\Delta_H^{(1)}$	stable	loss	$-\Delta_H^{(2)}$	stable	loss	$-\Delta_H^{(3)}$	stable	loss	$-\Delta_H^{(4)}$
0.032	0.9565258		11/3	0.9574761		13/4	0.9577929		13/4	
0.016	0.9575013	9/2	13/4	0.9577442	11/3	15/5	0.9578252	14/4	15/5	0.9578265
0.008	0.9577506	11/3	15/5	0.9578120	13/3	17/5	0.9578324	17/5	17/5	0.9578336
0.004	0.9578135	13/3	17/5	0.9578290	15/4	19/6	0.9578341	19/5	19/6	0.9578345
0.002	0.9578296	15/4	19/6	0.9578335	17/5	21/6	0.9578347	20/6	21/6	0.9578349
0.001	0.9578330	18/5	21/6	0.9578339	21/6	23/7	0.9578342	20/6	23/7	0.9578341
0.0005	0.9578341	19/5	23/7	0.9578357	18/5	25/8	0.9578363	18/5	25/8	0.9578345
0.00025	0.9578322	18/5	25/8	0.9578371	18/5	27/8	0.9578388	18/5	27/8	0.9578316
0.000125	0.9578405	16/4	27/8	0.9578352	16/4	29/9	0.9578334	16/4	29/9	0.9578432
6.25e–05	0.9578258	15/4	29/9	0.9577965	14/4	31/9	0.9577868	14/4	31/9	0.9578209
3.125e–05	0.9578342	14/4	31/9	0.9579019	12/3	33/10	0.9579244	12/3	33/10	0.9578370

Table 6. H$_2$ molecule, 837 ECG functions; $E_l = -1.1744759312$, $S_0 = 0.9999999999998710$, $N_{bits} = 42$

h	$-\Delta_H^{(1)}$	stable	loss	$-\Delta_H^{(2)}$	stable	loss	$-\Delta_H^{(3)}$	stable	loss	$-\Delta_H^{(4)}$
0.032	0.9570840		11/3	0.9580366		13/4	0.9583542		13/4	
0.016	0.9580618	9/2	13/4	0.9583053	11/3	15/5	0.9583865	14/4	15/5	0.9583877
0.008	0.9583116	11/3	15/5	0.9583731	13/3	17/5	0.9583936	17/5	17/5	0.9583948
0.004	0.9583747	13/3	17/5	0.9583901	15/4	19/6	0.9583953	19/5	19/6	0.9583957
0.002	0.9583905	15/4	19/6	0.9583943	17/5	21/6	0.9583955	21/6	21/6	0.9583958
0.001	0.9583943	17/5	21/6	0.9583957	19/5	23/7	0.9583962	20/6	23/7	0.9583956
0.0005	0.9583966	18/5	23/7	0.9583982	18/5	25/8	0.9583987	18/5	25/8	0.9583973
0.00025	0.9583976	18/5	25/8	0.9584106	16/4	27/8	0.9584149	15/4	27/8	0.9583980
0.000125	0.9584047	16/4	27/8	0.9584728	13/3	29/9	0.9584955	13/3	29/9	0.9584070
6.25e–05	0.9584114	14/4	29/9	0.9585891	12/3	31/9	0.9586483	12/3	31/9	0.9584136
3.125e–05	0.9588280	11/3	31/9	0.9588480	10/3	33/10	0.9588548	10/3	33/10	0.9589669

Table 7. Helium dimer, 2382 ECG functions; $E_l = -5.80748355$, $S_0 = 1.000000000002466$, $N_{bits} = 38$

h	$-\Delta_{He}^{(1)}$	stable	loss	$-\Delta_{He}^{(2)}$	stable	loss	$-\Delta_{He}^{(3)}$	stable	loss	$-\Delta_{He}^{(4)}$
0.032	6.0983722		8/2	6.1184141		10/3	6.1250948		10/3	
0.016	6.1184141	8/2	10/3	6.1235933	10/3	12/4	6.1253197	14/4	12/4	6.1250947
0.008	6.1235933	10/3	12/4	6.1249094	12/3	14/4	6.1253481	17/5	14/4	6.1253197
0.004	6.1249095	12/3	14/4	6.1252410	14/4	16/5	6.1253515	20/6	16/5	6.1253482
0.002	6.1252408	14/4	16/5	6.1253232	16/4	18/5	6.1253507	21/6	18/5	6.1253512
0.001	6.1253236	16/4	18/5	6.1253442	18/5	20/6	6.1253510	19/5	20/6	6.1253512
0.0005	6.1253447	18/5	20/6	6.1253308	17/5	22/7	6.1253261	17/5	22/7	6.1253517
0.00025	6.1253420	17/5	22/7	6.1253960	15/4	24/7	6.1254140	15/4	24/7	6.1253411
0.000125	6.1252862	15/4	24/7	6.1253025	13/3	26/8	6.1253079	13/3	26/8	6.1252677
6.25e–05	6.1248507	13/3	26/8	6.1231441	11/3	28/8	6.1225753	11/3	28/8	6.1247055
3.125e–05	6.1245067	11/3	28/8	6.1191938	9/2	30/9	6.1174233	9/2	30/9	6.1243920

gives the error proportional to h^4 and is not based on a vague assumption, but requires additional evaluation of wave functions for $Q + 2h$ and $Q - 2h$.

If the molecule is placed along one of the coordinate frame axes, two components of Δ_A are to be computed – parallel and perpendicular to the bond axis. In the present work, another orientation of the molecule has been chosen – the bond axis is a diagonal of the cube, whose 3 walls coincide with the coordinate frame planes. Only one Δ_Q integral is then needed, as $\Delta_{x,A}$, $\Delta_{y,A}$ and $\Delta_{z,A}$ are equal.

Due to the symmetry of hydrogen molecule and helium dimer, both atomic contributions are the same and only one is given in Tables 5-7. The symmetry projector in equation (20) doubles the numbers of "primitive" (i.e. non symmetry adapted) basis functions, but calculation of Δ_Q integrals was carried out with spatial symmetry disabled, so that the real expansion lengths amounted to 150 and 1674 for H$_2$, and 4764 for He···He. The latter system was described with the reoptimized 2400-term function [14], from which a few basis functions, which did not lower the energy, have been removed.

The convergence patterns in molecular calculations agree with these observed for atoms, although the impro-vement is a little smaller. Formula (19) gives usually up to 2-3 more stable bits than (12) and (13), but there are some cases, in which those equations seem to work better. For the hydrogen molecule, described with the 75-term wave function, formula (13) seems to give 21 stable bits, while (19) provides only 20 bits. However, formula (27), which should be regarded as the most accurate one, gives the value of Δ_H closer to that of (19) and its six significant digits of the result are stable in a wide range of h. Another example of a "false stability" appears for the helium dimer with equation (12), where 6 significant digits do not change in the value of $\Delta_{He} = 6.12534$, when h decreases from 0.0005 to 0.00025. This calculation has been carried out on the edge of real precision of 38 bits (15 bits lost, due to the numerical noise!) and the 6'th digit is incorrect – formulas (19) and (27) give a little larger $\Delta_{He} = 6.12535$. This example justifies the method of estimation of accuracy, which takes the number of certain bits in account and shows, that just counting the unchanging digits may be not sufficient.

The calculations for positronic lithium hydride mole-cule show, that a single value of h for both atoms would be suboptimal. The LiH molecule is highly polar and the

Table 8. Positronic LiH molecule, 2048 ECG functions; $E_l = -8.107864$, $S_0 = .9999999999993515$, $N_{bits} = 40$

h	$-\Delta_{Li}^{(1)}$	stable	loss	$-\Delta_{Li}^{(2)}$	stable	loss	$-\Delta_{Li}^{(3)}$	stable	loss	$-\Delta_{Li}^{(4)}$
0.032	15.1438384		7/2	15.2588572		9/3	15.2971968		9/3	
0.016	15.2588505	7/2	9/3	15.2890412	8/2	11/3	15.2991048	12/3	11/3	15.2971879
0.008	15.2890395	8/2	11/3	15.2967688	10/3	13/4	15.2993452	15/4	13/4	15.2991026
0.004	15.2967684	10/3	13/4	15.2987234	12/3	15/5	15.2993750	18/5	15/5	15.2993447
0.002	15.2987230	12/3	15/5	15.2992148	14/4	17/5	15.2993788	21/6	17/5	15.2993746
0.001	15.2992151	14/4	17/5	15.2993340	16/4	19/6	15.2993736	21/6	19/6	15.2993791
0.0005	15.2993365	16/4	19/6	15.2993497	19/5	21/6	15.2993541	19/5	21/6	15.2993770
0.00025	15.2993784	18/5	21/6	15.2993641	17/5	23/7	15.2993594	17/5	23/7	15.2993924
0.000125	15.2993011	17/5	23/7	15.2992115	15/4	25/8	15.2991815	15/4	25/8	15.2992754
6.25e–05	15.2993299	15/4	25/8	15.2992567	13/3	27/8	15.2992322	13/3	27/8	15.2993395
3.125e–05	15.2993633	13/3	27/8	15.2979549	11/3	29/9	15.2974853	11/3	29/9	15.2993744
h	$-\Delta_{H}^{(1)}$	stable	loss	$-\Delta_{H}^{(2)}$	stable	loss	$-\Delta_{H}^{(3)}$	stable	loss	$-\Delta_{H}^{(4)}$
0.032	1.2879212		10/3	1.2889341		12/4	1.2892718		13/4	
0.016	1.2889270	10/3	12/4	1.2891844	12/3	14/4	1.2892702	19/5	15/5	1.2892623
0.008	1.2891826	12/3	14/4	1.2892474	14/4	16/5	1.2892690	20/6	17/5	1.2892678
0.004	1.2892470	14/4	16/5	1.2892630	16/4	18/5	1.2892684	20/6	19/6	1.2892684
0.002	1.2892634	16/4	18/5	1.2892665	18/5	20/6	1.2892675	19/5	21/6	1.2892689
0.001	1.2892680	18/5	20/6	1.2892644	18/5	22/7	1.2892632	17/5	23/7	1.2892695
0.0005	1.2892639	18/5	22/7	1.2892578	16/4	24/7	1.2892558	15/4	25/8	1.2892625
0.00025	1.2892431	15/4	24/7	1.2892582	14/4	26/8	1.2892632	13/3	27/8	1.2892362
0.000125	1.2893067	14/4	26/8	1.2894130	12/3	28/8	1.2894485	11/3	29/9	1.2893279
6.25e–05	1.2890619	12/3	28/8	1.2888515	10/3	30/9	1.2887813	9/2	31/9	1.2889803
3.125e–05	1.2892509	10/3	30/9	1.2859543	8/2	32/10	1.2848559	7/2	33/10	1.2893139

presence of the positively charged positron, which is localized at the negative (*H*) end [15], causes its additional polarization − the bond length increases and the electron density moves towards the *H* nucleus. The lowest energy dissociation products of e^+LiH are positronium hydride and lithium cation. Close to the equilibrium distance, moving of the Li nucleus, surrounded by the compact distribution of its core electrons, gives most accurate approximation of Δ_{Li} integral at $h = 0.002$. On the other hand, Δ_H is very close to that of isolated PsH atom, which leptonic density is much more diffuse than that of Li$^+$ and the most accurate approximation is obtained at $h = 0.004$.

IV. CONCLUSIONS

The proposed method of calculation of adiabatic corrections, although not proven mathematically for molecules, seems to work well for all studied systems, which have different leptonic structures. It gives usually one additional stable significant digit, in comparison with Eqs. (12)

and (13), using the same wave functions. This extra stability is not a spurious effect, as the results are close to these of formula (27), which error certainly decreases as h^{-4}. The most stable values of Δ_A are obtained for larger shifts. The recommended value of h for the new algorithm is between 0.002 and 0.004 bohr.

One may ask, whether calculation of 6 instead of 5 significant decimal digits of the adiabatic correction is worth the effort of evaluation of additional overlap integrals for Eq. (19), or even wave functions for equation (27), if the result would be changed by a few nanohartrees. The answer is not unique. In most calculations, there would be no practical difference. Unfortunately, decreasing real precision is the price to be paid for the increasing accuracy of leptonic energies. The number of certain bits decreases with the expansion length of wave function (20) and with the number of light particles. Let us compare the two, 75- and 837-term wave functions of hydrogen molecule, which give the electronic energies accurate to a fraction microhartree and nanohartree, respectively, but with 44 and 42 cer-

tain bits. For the short function, the satisfactory accuracy of E_{ad} would be about 0.1 μhartree. Assuming the proton mass equal to 1836.15267 a.u., the value of 0.0005217 hartree is obtained. It requires only 4 stable significant digits of Δ_H, which can be easily calculated even with methods (12) or (13). However, for the long expansion we would like to compute the adiabatic correction with the accuracy comparable to that of electronic energy. The new method gives the value of 0.0005219585 hartree, with the last digit uncertain, which is acceptable, while two last digits would be uncertain, if one of older algorithms would be applied. In the case of larger systems, described with extensive wave functions, for which the loss of precision resulting from the numerical noise is significant, this additional significant digit may allow to avoid the time consuming calculation of E_{ad} with extended precision variables. The obvious target could be the helium dimer, for which calculations with very long expansions (up to 4800 ECG functions) have been carried out recently [16].

Another area of practical application of the new algorithm are the studies of positronic systems, in which the positron is treated as a light pseudonucleus with the charge less than 1 [17], within a modified adiabatic approximation. Due to small positron mass, the contribution of E_{ad} to the effective potential for positronic motion is comparable with that of electronic energy.

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