Relativistic correction to the helium dimer interaction energy

Wojciech Cencek
Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA

Jacek Komasa
Department of Chemistry, Quantum Chemistry Group, A. Mickiewicz University, Grunwaldzka 6, 60780 Poznań, Poland

Krzysztof Pachucki
Institute of Theoretical Physics, Warsaw University, Hoża 69, 00-681 Warsaw, Poland

Krzysztof Szalewicz
Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA
(Dated: December 1, 2005)

The lowest-order relativistic correction to the helium-helium interaction energy has been calculated for the first time, using two independent methods based on expansions in explicitly correlated Gaussian functions. At the equilibrium interatomic distance of 5.6 bohr, this correction amounts to $+15.4 \pm 0.6$ mK. As a by-product, a new upper bound of -10.9985 K for the nonrelativistic Born-Oppenheimer interaction energy has been obtained.

PACS numbers: 31.15.Ar, 31.30.Jv

One of the most thoroughly studied interactions is that involving two helium atoms, due to its role as a model of weak interactions and due to the ubiquitous presence of helium in physical and technological applications. Helium exhibits superfluidity and helium nanodroplets provide a medium for a fast developing branch of high-resolution spectroscopy [1, 2]. Since the depth of the interaction potential is only about 11 K, it can accommodate just one vibrational level. The bound state of $^4He_2$ was detected experimentally in 1993 [3]. According to recent measurements, the dissociation energy has an extremely small value of about 1 mK and the mean internuclear distance is as large as 50 Å [4]. The fact that the vibrational wave function is diffused over very large distances makes it sensitive to the details of the potential. Also new helium-based standards of temperature and pressure that were proposed [5], depend critically on the accuracy of *ab initio* potentials: an accuracy of the order of 1 mK is needed, which translates to 90 ppm of the interaction energy or just 0.5 ppb of the total dimer energy.

About ten years ago, the accuracy of the *ab initio* helium dimer potentials surpassed that of potentials derived from experimental data. The most recent value [6] of the potential well depth at the nonrelativistic Born-Oppenheimer (BO) level amounts to -11.009 ± 0.008 K (1 hartree=315774.65 K). The near-millikelvin accuracy reached means that various more advanced physical effects, not accounted for in typical electronic structure calculations, can no longer be neglected. The diagonal adiabatic correction of -0.013 K (for $^4He_2$) was calculated from explicitly correlated Gaussian (ECG) wave functions [7]. On the other hand, virtually no information (not even the sign) on the relativistic effect has been available. The difficulty stems from the fact that the relativistic contribution to the interaction energy is so small that the dimer and monomer energies have to be computed with at least 5 significant digits. Currently, the only possibility to achieve such a high accuracy is to use large expansions of explicitly correlated wave functions in association with special techniques to accelerate the convergence of the singular relativistic operators.

The variational BO wave functions have been chosen in the ECG form

$$\Psi = \hat{O}^N_{\rm as}\left\{\Xi^{N,S,M_S}\hat{P}\left[c_0\phi_0 + \sum_{k=1}^{M} c_k\phi_k(1,2,\dots N)\right]\right\}, \tag{1}$$

where $\hat{O}^N_{\rm as}$ is the N-electron antisymmetrizer, Ξ^{N,S,M_S} is one of the N-electron spin functions corresponding to spin quantum numbers S and M_S, $\hat{P}$ is the point group symmetry projector, and c_k are variational parameters. For the singlet ground state of the helium dimer,

$$\Xi^{4,0,0} = [\alpha(1)\beta(2) - \beta(1)\alpha(2)]\,[\alpha(3)\beta(4) - \beta(3)\alpha(4)] \tag{2}$$

and $\hat{P} = \frac{1}{2}(1 + \hat{\imath})$, where $\hat{\imath}$ is the inversion through the geometrical center. In Eq. (1), $\phi_0 \equiv 0$, except in the "monomer contraction" scheme, described later, and $\phi_k(1,2,\dots N)$ denotes N-electron ECG functions

$$\phi_k(1,2,\dots N) = \prod_{i=1}^{N} e^{-\alpha_{ki}|\boldsymbol{r}_i - \boldsymbol{A}_{ki}|^2} \prod_{i>j=1}^{N} e^{-\beta_{kij}|\boldsymbol{r}_i - \boldsymbol{r}_j|^2}, \tag{3}$$

where α_{ki}, β_{kij}, and $\mathbf{A}_{ki}$ are nonlinear variational parameters. The functions defined by Eqs. (1) and (3) have been used with much success for a number of two-, three-, and four-electron systems (see Ref. [8] and references therein). Note that in the case of N=2, the ECG functions of Eq. (3) are commonly called Gaussian-type geminals (GTG). All the nonlinear parameters contained in ϕ_k are randomly generated and then carefully optimized with respect to the nonrelativistic BO energy of the dimer, E_0 (see Ref. [9] for details of the optimization algorithm). The linear parameters c_k are found by solving the usual system of secular equations in each call to the energy calculation routine.

The lowest-order relativistic correction to the energy, E_2, can be calculated as the expectation value of the Breit-Pauli Hamiltonian [10], which, for singlet states of a four-electron system, takes the following form:

$$\hat{H}_{\mathrm{BP}} = c^{-2}(\hat{H}_1 + \hat{H}_2 + \hat{D}_1 + \hat{D}_2), \tag{4}$$

where

$$\hat{H}_1 = -\frac{1}{8}\sum_{i=1}^{4} p_i^4, \tag{5}$$

$$\hat{H}_2 = -\frac{1}{2}\sum_{i<j=1}^{4} \frac{1}{r_{ij}}\left(\boldsymbol{p}_i\boldsymbol{p}_j + \frac{\boldsymbol{r}_{ij}(\boldsymbol{r}_{ij}\boldsymbol{p}_i)\boldsymbol{p}_j}{r_{ij}^2}\right), \tag{6}$$

$$\hat{D}_1 = \frac{\pi}{2}\sum_{A}\sum_{i=1}^{4} Z_A\delta(\boldsymbol{r}_i - \boldsymbol{A}), \tag{7}$$

$$\hat{D}_2 = \pi\sum_{i<j=1}^{4}\delta(\boldsymbol{r}_{ij}). \tag{8}$$

In the above, c=137.03600 a.u. is the speed of light, $\boldsymbol{p}_i$ is the momentum operator of electron i, $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, Z_A is the charge of nucleus A located at the point $\boldsymbol{A}$, and δ is the Dirac delta function. For the interaction expectation values we will use notation: $\Delta X = X_{\mathrm{dimer}} - 2X_{\mathrm{monomer}}$. In all the calculations, the equilibrium internuclear distance of 5.6 bohr was assumed.

To obtain reliable error estimates, we used two different methods of computation, which we will refer to as integral transform (IT) and monomer contraction (MC). **The integral transform method** was recently introduced by three of us [11] as a remedy for the notorious problem of the very slow convergence of expectation values of relativistic operators computed using Gaussian basis sets. The idea is to transform the integrals with singular operators to a form allowing the singular parts to be integrated using exact asymptotic formulas. For example, the $\langle\delta(\boldsymbol{r})\rangle$ expectation value, after using the Poisson equation and the Laplace transform of $1/r$, can be expressed as

$$\langle\Psi|\delta(\boldsymbol{r})|\Psi\rangle = \frac{1}{2\pi^{3/2}}\int_0^\infty \langle\Psi|2t^2(3-2t^2r^2)e^{-t^2r^2}|\Psi\rangle\, dt. \tag{9}$$

The expectation value on the right-hand side, $f(t)$, converges quickly with increasing size of the expansion of Ψ, except for large values of t. In the latter region, an asymptotic formula resulting from the Kato cusp condition fulfilled by the exact wave function is used instead to evaluate $f(t)$.

We first performed calculations *without* applying the IT technique. Table I contains the values of the nonrelativistic and relativistic components of the interaction energy, obtained in all the cases by subtracting the (virtually exact) literature values for the helium atom [12]. Note that because no unambiguous relation between the floating-center 4-electron dimer and atom-centered 2-electron monomer ECG functions can be formulated (in contrast to the traditional orbital basis functions), it is not possible to use the counterpoise corrected approach, *i.e.*, to perform calculations for both the dimer and the monomer in the same basis set. The values of ΔE_0 represent strict upper bounds to the exact nonrelativistic interaction energy. The lowest one, -10.9953 K, is significantly more accurate than the best previously published variational result, -10.981 K [13], but still too small in magnitude to fit within the error bars established in Ref. [6]: -11.009 ± 0.008 K. The convergence of the relativistic properties, calculated directly from Eqs. (5)–(8), is poor (with the exception of $c^{-2}\Delta H_2$). However, due to large cancelations between the $c^{-2}\Delta H_1$ and $c^{-2}\Delta D_1$ contributions, the value of ΔE_2 converges reasonably fast.

Table II presents the results for the "difficult" relativistic contributions obtained with the IT regularization procedure. Comparison with Table I shows that the regularization results in a dramatic improvement of the accuracy, yielding values converged to about 0.1 mK in all the three cases (judging from the rate of convergence). Whereas the final value of ΔE_2 seems to be saturated to better than 0.1 mK, the irregularities in the convergence pattern of $c^{-2}\Delta H_1$ and the fact that the optimization of our 4800-term expansion was not as extensive as in the case of the shorter expansions demand some caution. We assume that the difference between the complete basis set limit value of ΔE_2 and the M=4800 result can be as much as twice the difference between the M=4800 and M=2400 results and assign the same value to the uncertainty of the estimated limit. Thus, our estimated exact value of ΔE_2 from the IT calculations is $+15.4\pm0.2$ mK.

The success of the IT method is due to the fact that in the r.h.s. of Eq. (9) (and its analogue for p^4) the expectation value of a global operator is calculated, rather than of the highly singular $\delta(\boldsymbol{r})$ operator. It should be noted here that several other possibilities of applying global properties to evaluate relativistic corrections exist (see Ref. [11] for an example). In many cases, the direct perturbation theory (DPT) [14, 15] provides a method which converges faster than the method using the Breit-Pauli Hamiltonian (4). However, the two-electron ΔD_2 term, the most slowly convergent contribution in our calculations, is the same in both methods, so that the use of DPT would not help.

The idea of the second approach, **the monomer contraction method**, is based on the fact that, because of the very small value of the interaction energy, the wave function of the helium dimer is not very different from the product of the wave functions of the noninteracting monomers. It is logical, therefore, to include such a product—which can be constructed with a high accuracy—as a frozen part of a dimer function and optimize only the remaining part. Thus, taking a high-quality helium atom ECG function

$$\Psi_{\rm He} = \hat{O}^2_{\rm as}\left\{[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\sum_{l=1}^{L} d_l\phi_l(1,2)\right\}, \tag{10}$$

we define the function ϕ_0 in Eq. (1) as

$$\phi_0 = \sum_{l=1}^{L}\sum_{m=l}^{L} d_l d_m \phi_l^A(1,2)\phi_m^B(3,4), \tag{11}$$

where the functions $\phi_l^X(i,j)$ have the form of Eq. (3), with the centers $\boldsymbol{A}_{ki}$ restricted to the location of nucleus A or B. The $(L^2{+}L)/2$ four-electron terms resulting from Eq. (11) have the same form of Eq. (3) as the remaining M terms, but the part denoted by ϕ_0 is treated as a contraction with one common linear coefficient, c_0, and does not undergo any optimization with respect to the dimer energy.

As the atomic function of Eq. (10), we used a carefully optimized 283-term expansion yielding the nonrelativistic energy of the two monomers with an error of only 0.08 mK. Longer ECG expansions for the helium atom can easily be obtained but their use in our MC scheme would be problematic due to prohibitive cost and accumulation of numerical errors resulting from the very large number of the product terms of Eq. (11). A 141-term expansion was used as a check (the L=141 contraction was added to M terms optimized in the presence of the L=283 contraction). The relevant helium atom expectation values calculated with these two functions are listed in Table III and compared with the exact values from Ref. [12].

Using the MC procedure, we generated several ECG expansions up to M=1200. The inclusion of the monomer product results in a much faster convergence of ΔE_0 and the (L=283, M=1200) function yields a value of −10.9985 K, significantly lower than the regular 4800-term ECG expansion. If the exact helium atom values from Ref. [12] are subtracted to get the relativistic contributions, the results are very poor and ΔE_2 appears to converge to 0.020 K (for L=283) or 0.034 K (for L=141). However, with the MC wave functions, we do not have to subtract the exact atomic values. Let us briefly analyze such functions. Since the error of E_0 for two helium atoms described by the 283-term expansions is five orders of magnitude smaller than ΔE_0, the minimization of E_0 for the dimer is (in the range of M used by us) directed entirely towards optimizing the interaction part. Thus, the atomic components remain unchanged in the dimer wave function and, consequently, the monomer contributions in E_2 are at the level of the L-term monomer expansion. Therefore, in this case it is completely adequate to subtract the monomer properties *calculated with the function used to build the contraction* instead of the exact values. This claim is confirmed by the results in Table IV, which practically do not depend on the value of L. The best values of $c^{-2}\Delta D_1$ and $c^{-2}\Delta D_2$ are in excellent agreement with the IT predictions. The values of $c^{-2}\Delta H_1$, however, seem to converge here to a slightly higher limit, which is consistent with the irregularities noted in Table II. Since the convergence of ΔE_2 is not as regular as in the IT calculations, we did not attempt to extrapolate the MC results. However, the MC results may indicate that the basis set limit of ΔE_2 is somewhat larger than the prediction from the IT method, perhaps as large as 0.0160 K (the L=283, M=1200 result plus twice the difference between the M=1200 and 600 values). Therefore, we have enlarged the error bars established for the IT result to encompass this value. Thus, our final recommended value of ΔE_2 is $+15.4 \pm 0.6$ mK. ΔE_2 is strongly dominated by the Breit term of Eq. (6), as the one-electron terms cancel each other to a large extent and the effect of the two-electron δ term is negligible.

Obviously, the most accurate method would be the combination of both our approaches, *i.e.*, calculating all the expectation values with the ECG functions containing monomer contractions, using the regularized IT expressions. However, this solution is currently too expensive because the IT scheme involves time-consuming numerical integration of the function $f(t)$ in Eq. (9).

Our values of the nonrelativistic BO interaction energy in Tables I and IV seem to converge to a value slightly below −11.000 K, which agrees with our recent result of -11.009 ± 0.008 K [6] and yields another confirmation of the fact that few-millikelvin accuracy has been reached for this quantity. Thus, our present calculation of the relativistic correction removes the largest current source of uncertainty in the helium dimer interaction energy. The only unknown contribution which can be relevant is that of the quantum electrodynamics. Judging from the fact that the QED correction to the helium atom polarizability is 22 ppm [16] whereas the analogous relativistic correction is −58 ppm [17, 18], one can expect the QED effect on the interaction energy to be also smaller than the relativistic effect. Nevertheless, it is probably not negligible and its accurate calculation seems desirable.

This work was supported by a grant from NIST and the NSF grant CHE-0239611. We thank Mike Moldover for numerous discussions. JK acknowledges the support from the Polish State Committee for Scientific Research grant SPB/COST/T-09/DWM 572 and from Poznań Supercomputing and Networking Center.

[1] J. P. Toennies and A. F. Vilesov, Annu. Rev. Phys. Chem. **49**, 1 (1998).
[2] C. Callegari, K. K. Lehmann, R. Schmied, and G. Scoles, J. Chem. Phys. **115**, 10090 (2001).
[3] F. Luo, G. McBane, G. Kim, C. F. Giese, and W. R. Gentry, J. Chem. Phys. **98**, 3564 (1993).
[4] R. E. Grisenti, W. Schöllkopf, J. P. Toennies, G. C. Hegerfeldt, T. Kohler, and M. Stoll, Phys. Rev. Lett. **85**, 2284 (2000).
[5] T. J. Buckley, J. Hamelin, and M. R. Moldover, Rev. Sci. Instrum. **71**, 2914 (2000); M. R. Moldover, J. Res. Natl. Inst. Stand. Technol. **103**, 167 (1998); J. J. Hurly and M. R. Moldover, *ibid.* **105**, 667 (2000).
[6] W. Cencek, M. Jeziorska, R. Bukowski, M. Jaszuński, B. Jeziorski, and K. Szalewicz, J. Phys. Chem. A **108**, 3211 (2004).
[7] J. Komasa, W. Cencek, and J. Rychlewski, Chem. Phys. Lett. **304**, 293 (1999). A newer calculation (J. Komasa and W. Cencek, unpublished) gives a value of -0.009 K.
[8] J. Rychlewski and J. Komasa, *Explicitly correlated functions in variational calculations* in: J. Rychlewski (Ed.) *Explicitly Correlated Wave Functions in Chemistry and Physics* (Kluwer, Dordrecht, 2003), p. 91.
[9] W. Cencek, J. Komasa, and J. Rychlewski, Chem. Phys. Lett. **246**, 417 (1995).
[10] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems*, Springer-Verlag, Berlin and New York (1957).
[11] K. Pachucki, W. Cencek, and J. Komasa, J. Chem. Phys. **122**, 184101 (2005).
[12] G. W. Drake, Nucl. Instr. Meth. Phys. Res. **B31**, 7 (1988).
[13] J. Komasa, J. Chem. Phys. **115**, 158 (2001).
[14] A. Rutkowski, J. Phys. B **19**, 149 (1986); **19**, 3431 (1986); **19**, 3443 (1986).
[15] W. Kutzelnigg, Z. Phys. D **11**, 15 (1989); **15**, 27 (1990).
[16] G. Łach, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. **92**, 233001 (2004).
[17] K. Pachucki and J. Sapirstein, Phys. Rev. A **63**, 012504 (2001).
[18] W. Cencek, K. Szalewicz, and B. Jeziorski, Phys. Rev. Lett. **86**, 5675 (2001).

TABLE I: Convergence of interaction energy components (in kelvins) with basis set size M using conventional approach.

M	ΔE_0	$c^{-2}\Delta H_1$	$c^{-2}\Delta H_2$	$c^{-2}\Delta D_1$	$c^{-2}\Delta D_2$	ΔE_2
300	-9.5279	1.5265	0.01351	-1.4907	0.0554	0.1047
600	-10.7560	0.6797	0.01381	-0.6652	0.0225	0.0508
1200	-10.9582	0.3278	0.01387	-0.3197	0.0114	0.0334
2400	-10.9900	0.2819	0.01388	-0.2757	0.0070	0.0271
4800	-10.9953	0.2232	0.01388	-0.2184	0.0049	0.0236

TABLE II: Convergence of interaction energy components (in kelvins) with basis set size M using IT regularization.

M	$c^{-2}\Delta H_1$	$c^{-2}\Delta D_1$	$c^{-2}\Delta D_2$	ΔE_2 [a]
300	0.0067	-0.0508	0.0131	-0.0175
600	0.0071	-0.0134	0.0025	0.0100
1200	0.0070	-0.0070	0.0004	0.0143
2400	0.0073	-0.0060	-0.0001	0.0151
4800	0.0074	-0.0059	-0.0002	0.0152

[a]Calculated using $c^{-2}\Delta H_2$ from Table I.

TABLE III: Expectation values of He calculated from the L-term atomic wave functions (in atomic units). $E_0' = -(E_0 + 2.903724) \times 10^{10}$.

L	E_0'	$\langle H_1 \rangle$	$\langle H_2 \rangle$	$\langle D_1 \rangle$	$\langle D_2 \rangle$
141	37109	-13.512142	-0.13909510	11.365569	0.334443
283	37690	-13.519197	-0.13909473	11.372486	0.334173
exact	37703	-13.522017	-0.13909469	11.375263	0.334094

TABLE IV: Convergence of interaction energy components (in kelvins) with basis set size M. L denotes the number of terms in the monomer expansion, see Eqs. (10) and (11). The values of ΔE_2 in the last column assume $c^{-2}\Delta H_2$=0.01388 K. The results are obtained by subtracting the helium atom expectation values computed for the monomer (with L terms) from those computed for the dimer.

M	ΔE_0	$c^{-2}\Delta H_1$	$c^{-2}\Delta D_1$	$c^{-2}\Delta D_2$	ΔE_2
			L=141		
0	10.5789	-0.0159	0.0135	0.0011	0.0126
128	-10.8296	0.0031	-0.0036	-0.0002	0.0132
300	-10.9675	0.0072	-0.0056	-0.0002	0.0153
600	-10.9911	0.0073	-0.0056	-0.0002	0.0154
1200	-10.9986	0.0078	-0.0058	-0.0002	0.0157
			L=283		
0	10.5790	-0.0159	0.0135	0.0011	0.0125
128	-10.8295	0.0031	-0.0036	-0.0002	0.0132
300	-10.9675	0.0070	-0.0056	-0.0002	0.0152
600	-10.9911	0.0074	-0.0057	-0.0002	0.0154
1200	-10.9985	0.0078	-0.0058	-0.0002	0.0156