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Electron affinities of small linear carbon clusters. Coupled cluster calculations with first-order correlation orbitals

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Electron affinities of the C_3 , C_4 , C_5 , and C_6 linear clusters are theoretically determined using an *ab initio* procedure which combines the first-order correlation orbital method and the coupled cluster method. The theoretical values 1.58, 3.41, 2.43, and 3.69 e.V. for C_3 , C_4 , C_5 , and C_6 , respectively, are systematically lower than the experimental estimates of Smalley *et al.* [Chem. Phys. Lett. **144**, 431 (1988)] (1.95, 3.70, 2.80, and 4.10 e.V.); however, the trends corresponding to the odd-even numbered chain alternation and to the increase of the size of the cluster are very similar.

I. INTRODUCTION

The calculation of the electron affinities (EA) for both atoms and molecular species is notoriously one of the most difficult tasks in quantum chemistry.¹ Many calculations have indicated that in order to reproduce reliably the experimental results within a few tenths of the electron volt, one has to apply an extended bases set and, most importantly, capture a very high percentage of the electron correlation energy. Since the electron attachment changes the number of electrons in the system, a size extensive theoretical treatment, such as that guaranteed by the many-body perturbation theory (MBPT) or the coupled cluster (CC) method, is essential.

Many reports have recently appeared concerning the formation and spectroscopic properties of pure carbon clusters.²⁻⁶ It has been well documented that carbon clusters of different sizes and shapes exhibit considerable electron affinities.^{7,8} In a recent paper, Smalley *et al.*⁷ report estimations of the electron affinities of carbon clusters (chains and rings) ranging from two to 30 atoms. Smalley's data, obtained by means of ultraviolet photoelectron spectroscopy (UPS), indicate that the even-numbered chains having open-shell electronic structures possess significantly higher electron affinities in comparison to the odd-numbered chains, which have closed-shell electronic structure in the ground state.

In the present report, we present theoretical *ab initio* calculations of the electron affinities of small carbon chains C_3 – C_6 . The calculations have been performed with the methodology which combines the first-order correlation orbital (FOCO) method for the open-shell systems developed recently in our group⁹ and the CCSD + T (CCSD) implementation of the coupled cluster method.¹⁰ The CCSD + T (CCSD) model exploits the fact that a final single iteration for the triple excitations using the T_2 amplitudes from the converged CCSD calculation is usually a quite accurate approximation to the iterative CCSDT-1 model that allows T_3 amplitudes to affect the value of the T_1 and T_2 amplitudes. Since the evaluation of the triple excitation contribution is the rate determining step in most CC/MBPT calculations, the T(CCSD) model is much more expeditious computationally, especially for larger molecular systems.

II. METHODOLOGY

Typically, any high-order correlation calculations on open-shell systems are considerably more time consuming than similar calculations on closed-shell systems. This is also the case for all implementations of the coupled cluster method, which for the open-shell systems are usually based on the spin unrestricted Hartree-Fock (SUHF) reference wave function, although some implementations permit the restricted open-shell Hartree-Fock reference. Different sets of orbitals for α and β electrons in the UHF reference function imply that there are two different sets of T_1 amplitudes [$T_1(\alpha)$, $T_1(\beta)$] and three sets of T_2 amplitudes [$T_2(\alpha\alpha)$, $T_2(\beta\beta)$, and $T_2(\alpha\beta)$], which correspond to excitations from occupied orbitals to the α and β virtual orbitals (correlation orbitals). The computation time for a CC calculation depends very strongly on the number of correlation orbitals (for a single iteration of the CCSDT-1 method, the rate factor scales as n_{corr}^4) and, therefore, only smaller systems can be calculated at this level of theory, but even for smaller systems, one can only afford to use only relatively small basis sets, which may lead to a lack of balance between the high level of the sophistication of the method and the error resulting from a severe incompleteness of the orbital space. This problem has been recently addressed in our work,⁹ which presented the FOCO scheme based on the UHF zero-order wave function Ψ_{UHF} . The method proposed there leads to contractions of the α and β correlation orbital spaces. The contraction scheme is based on the minimization of the second-order Hylleraas functional

$$E^2 \leq \langle \Psi^1 | H^0 - E^0 | \Psi^1 \rangle + 2 \langle \Psi^1 | V | \Psi_{\text{UHF}} \rangle \equiv J^2 \quad (1)$$

(Ψ^1 —the first-order correlation wave function, H^0 —the sum of the UHF Fock operators, E^0 —the sum of α and β occupied orbital energies $V = H - H^0$), which constitutes an upper bound to the second-order correlation energy, in the selected spaces of active α and β correlation orbitals. During the optimization process, the active orbitals are mixed with the nonactive orbitals in order to minimize the value of the Hylleraas functional. Since the orbital rotation is performed only among the virtual orbitals resulting from the UHF calculation, the separation between the occupied and virtual spaces remains intact. The parameters which represent the unitary orbital rotations (U_α and U_β matrices) in

TABLE I. Geometries of the linear carbon clusters used in the calculations.

	C ₃					
	●	—	●	—	●	$R = 1.3027 \text{ \AA}$
		R_2		R_1	R_2	
	●	—	●	—	●	$R_1 = 1.2959 \text{ \AA}$
		R_2		R_1	R_2	$R_2 = 1.3127 \text{ \AA}$
	●	—	●	—	●	$R_1 = 1.2872 \text{ \AA}$
		R_2		R_1	R_2	$R_2 = 1.2942 \text{ \AA}$
	●	—	●	—	●	$R_1 = 1.2812 \text{ \AA}$
		R_3		R_2	R_3	$R_2 = 1.2940 \text{ \AA}$
	●	—	●	—	●	$R_3 = 1.3008 \text{ \AA}$
		R_3		R_2	R_3	

our procedure are represented in an exponential form with antisymmetric matrices R_α and R_β :

$$U_\alpha = \exp(R_\alpha), \quad U_\beta = \exp(R_\beta),$$

$$(R_\alpha)^T = -R_\alpha, \quad (R_\beta)^T = -R_\beta. \quad (2)$$

This approach has been borrowed from the MCSCF problems.¹¹⁻¹³ The value of the rotation parameters is determined using the iterative Newton-Raphson technique which requires evaluation of the gradient and the Hessian matrices, i.e., the first and the second derivatives of the second-order functional with respect to the orbital rotation pa-

rameters R_α and R_β . In the UHF case, we generate the gradient and the Hessian separately for the α and β correlation orbitals. The converged active first-order correlation orbitals are subsequently used in the coupled cluster calculations. For the complete description of the procedure, we refer the reader to Ref. 9.

The following steps describe the computational scheme which was applied for determining the electron affinities of carbon chains:

(i) The molecular geometries for C₃, C₄, and C₆ have been optimized at the MBPT(2)/6-31G* level using the

TABLE II. C₆/C₅⁻. Minimization of the second-order Hylleraas functional for different sizes of the correlation orbital space. Energies in atomic units.

Occupied orbitals													
Symmetries			σ_g	π_{ux}	π_{uy}	δ_g	σ_u	π_{gx}	π_{gy}	δ_u			
C ₅	α		6	1	1	0	5	1	1	0			
	β		6	1	1	0	5	1	1	0			
C ₅ ⁻	α		6	2	1	0	5	1	1	0			
	β		6	1	1	0	5	1	1	0			
Number of FOCOs (orbital symmetry distribution)													
Second-order functional (percentage with respect to the second-order energy for the full space)													
(1)	C ₅	α	90	(27	10	10	3	22	8	8	2)	Full space	-0.672 638
		β	90	(27	10	10	3	22	8	8	2)		(100%)
	C ₅ ⁻	α	89	(27	9	10	3	22	8	8	2)	Full space	-0.632 164
		β	90	(27	10	10	3	22	8	8	2)		(100%)
(2)	C ₅	α	17	(5	2	2	1	4	1	1	1)		-0.387 654
		β	17	(5	2	2	1	4	1	1	1)		(57.6%)
	C ₅ ⁻	α	16	(5	1	2	1	4	1	1	1)		-0.324 772
		β	17	(5	2	2	1	4	1	1	1)		(51.4%)
(3)	C ₅	α	25	(7	3	3	1	4	1	1	1)		-0.494 093
		β	25	(7	3	3	1	4	1	1	1)		(73.5%)
	C ₅ ⁻	α	24	(7	2	3	1	4	1	1	1)		-0.433 857
		β	25	(7	3	3	1	4	1	1	1)		(68.6%)
(4)	C ₅	α	34	(9	4	4	1	7	4	4	1)		-0.587 166
		β	34	(9	4	4	1	7	4	4	1)		(87.3%)
	C ₅ ⁻	α	33	(9	3	4	1	7	4	4	1)		-0.533 062
		β	34	(9	4	4	1	7	4	4	1)		(84.3%)
(5)	C ₅	α	39	(11	5	5	1	9	4	4	1)		-0.615 183
		β	39	(11	5	5	1	9	4	4	1)		(91.5%)
	C ₅ ⁻	α	38	(11	4	5	1	9	4	4	1)		-0.569 159
		β	39	(11	5	5	1	9	4	4	1)		(90.0%)
(6)	C ₅	α	53	(15	6	6	2	13	5	5	1)		-0.655 706
		β	53	(15	6	6	2	13	5	5	1)		(97.5%)
	C ₅ ⁻	α	52	(15	5	6	2	13	5	5	1)		-0.611 711
		β	53	(15	6	6	2	13	5	5	1)		(96.8%)

GAUSSIAN86 program.^{14,15(a)} For C_5 , we used the geometry obtained in the CC optimization.^{15(b)} The structural parameters are presented in Table I. Since we are concerned with the vertical electron affinities, the geometries for the anions were the same as for the respective neutral systems.

(ii) Self-consistent-field (UHF/SCF) calculations were performed for the neutral and the anionic systems using the $4s2p$ Gaussian basis set of Dunning¹⁶ augmented with the d polarization function (exponent = 0.654) of Redmon *et al.*,¹⁷ two additional s (exponents = 0.06 and 0.02), and one p (exponent = 0.0438) diffuse orbitals.

(iii) Selective integral transformations were performed to generate three sets of molecular integrals $\langle i_\alpha j_\alpha | a_\alpha b_\alpha \rangle$, $\langle i_\beta j_\beta | a_\beta b_\beta \rangle$, $\langle i_\alpha j_\beta | a_\alpha b_\beta \rangle$, where $i_\alpha, j_\alpha, \dots$ and i_β, j_β, \dots indices indicate occupied UHF orbitals and $a_\alpha, b_\alpha, \dots$ and a_β, b_β, \dots indicate virtual UHF orbitals. The integral sets were subsequently used to optimize FOCOs for the α and β electrons.

(iv) In the FOCO optimization, one has to decide about the number of the active correlation orbitals. Obviously, the more orbitals one includes in the active space, the closer the value of the second-order functional resembles the second-

order energy which one obtained with all virtual orbitals. Also, since in the FOCO optimization we fully employed the molecular symmetry, i.e., only orbitals which belong to the same symmetry representations are mixed, one needs to decide on the symmetry distribution of the correlation orbitals. There is no obvious way to make this selection other than by performing some FOCO optimization and choosing the active correlation space based on the analysis of the results. One encounters a similar problem in the MCSCF calculations. In our calculations, the total number of active orbitals (occupied plus correlation) had to be the same for the α and β electrons—the limitation dictated by the CC program PROPAGATOR¹⁸ used in the present studies. We also used the same total number of orbitals for the neutral system as for the respective anion. This last restriction could produce some inadequacy in the description of the correlation for the neutral and anionic systems, because within the same number of orbitals, the anion with one extra electron would have one more occupied orbital and, consequently, one less correlation orbital than the neutral.

Since the present study is the first practical use of the

TABLE III. C_6/C_6^- . Minimization of the second-order Hylleraas functional for different sizes of the correlation orbital space. Energies in atomic units.

Occupied orbitals										
Symmetries			σ_g	π_{ux}	π_{uy}	δ_g	σ_u	π_{gx}	π_{gy}	δ_u
C_6	α	7	2	2	0	6	1	1	0	
	β	7	1	1	0	6	1	1	0	
C_6^-	α	7	2	2	0	6	1	1	0	
	β	7	2	1	0	6	1	1	0	

Number of FOCOs (orbital symmetry distribution)													
Second-order functional (percentage with respect to the second-order energy for the full space)													
(1)	C_6	α	107	(29	10	10	3	30	11	11	3)	Full space	− 0.738 051
		β	109	(29	11	11	3	30	11	11	3)		(100%)
	C_6^-	α	107	(29	10	10	3	30	11	11	3)	Full space	− 0.798 521
		β	108	(29	11	11	3	30	11	11	3)		(100%)
(2)	C_6	α	22	(7	1	1	1	7	2	2	1)		− 0.424 232
		β	24	(7	2	2	1	7	2	2	1)		(57.5%)
	C_6^-	α	22	(7	1	1	1	7	2	2	1)		− 0.455 246
		β	23	(7	1	2	1	7	2	2	1)		(57.0%)
(3)	C_6	α	30	(9	2	2	1	9	3	3	1)		− 0.538 528
		β	32	(9	3	3	1	9	3	3	1)		(73.0%)
	C_6^-	α	30	(9	2	2	1	9	3	3	1)		− 0.572 035
		β	31	(9	2	3	1	9	3	3	1)		(71.6%)
(4)	C_6	α	38	(10	4	4	1	10	4	4	1)		− 0.617 571
		β	40	(10	5	5	1	10	4	4	1)		(83.7%)
	C_6^-	α	38	(10	4	4	1	10	4	4	1)		− 0.662 494
		β	39	(10	4	5	1	10	4	4	1)		(83.0%)
(5)	C_6	α	46	(12	5	5	1	12	5	5	1)		− 0.663 894
		β	48	(12	6	6	1	12	5	5	1)		(90.0%)
	C_6^-	α	46	(12	5	5	1	12	5	5	1)		− 0.712 483
		β	47	(12	5	6	1	12	5	5	1)		(89.2%)
(6)	C_6	α	64	(17	6	6	2	17	7	7	2)		− 0.721 593
		β	66	(17	7	7	2	17	7	7	2)		(97.8%)
	C_6^-	α	64	(17	6	6	2	17	7	7	2)		− 0.777 409
		β	65	(17	6	7	2	17	7	7	2)		(97.4%)
(7)	C_6	α	74	(20	7	7	2	20	8	8	2)		− 0.728 044
		β	76	(20	8	8	2	20	8	8	2)		(98.6%)
	C_6^-	α	74	(20	7	7	2	20	8	8	2)		− 0.785 695
		β	75	(20	7	8	2	20	8	8	2)		(98.4%)

TABLE IV. MBPT/CC energies for C_5/C_5^- and C_6/C_6^- obtained with FOCOs. Energies in atomic units.

	C_5	C_5^-	C_6	C_6^-
SCF	-189.037 067	-189.145 610	-226.884 606	-226.980 903
MBPT(2)	-0.672 638	-0.632 164	-0.738 051	-0.798 521
Calculations with FOCOs				
Number of FOCOs				
α	39	38	38	38
β	39	39	40	39
Correlation energy				
MBPT(2)	-0.615 183	-0.569 159	-0.617 571	-0.662 494
MBPT(3)	-0.611 695	-0.589 018	-0.643 913	-0.671 834
CCSD	-0.623 223	-0.607 383	-0.659 34	-0.685 762
CCSD + T(CCSD)	-0.663 466	-0.636 058	-0.687 677	-0.714 566
E_{corr}^a	-0.720 921	-0.699 063	-0.808 157	-0.850 593
$E_{\text{corr}}^{\text{SC}^b}$	-0.725 430	-0.706 469	-0.821 834	-0.861 285
Largest coupled cluster amplitudes				
t_1	-0.043	0.136	0.103	-0.107
t_2	-0.091	-0.082	-0.083	0.107

^aCalculated using Eq. (3).^bCalculated using Eqs. (3) and (4a).

UHF/FOCO/CC technique, we performed FOCO optimization for several different sizes and symmetry distributions of the active correlation space for the C_5 and C_6 molecules. The results are presented in Tables II and III for C_5 and C_6 ,

respectively. Upon examining the results, one sees that when slightly more than half of all virtual orbitals are included in the active correlation space, the value of the second-order functional exceeds 97% of the second-order energy deter-

TABLE V. C_3/C_3^- and C_4/C_4^- . Minimization of the second-order Hylleraas functional. Energies in atomic units.

Symmetries		Occupied orbitals										
		σ_g	π_{ux}	π_{uy}	δ_g	σ_u	π_{gx}	π_{gy}	δ_u			
C_3	α	4	1	1	0	3	0	0	0			
	β	4	1	1	0	3	0	0	0			
C_3^-	α	4	1	1	0	3	1	0	0			
	β	4	1	1	0	3	0	0	0			
C_4	α	5	1	1	0	4	1	1	0			
	β	5	1	1	0	4	0	0	0			
C_4^-	α	5	1	1	0	4	1	1	0			
	β	5	1	1	0	4	1	0	0			
Number of correlation orbitals (symmetry distribution)												
C_3	α	54	(17	6	6	2	12	5	5	1)	Full space	- 0.382 223 (100%)
	β	54	(17	6	6	2	12	5	5	1)		
C_3^-	α	54	(17	6	6	2	12	5	5	1)	Full space	- 0.366 342 (100%)
	β	58	(17	6	6	2	12	4	5	1)		
C_3	α	26	(7	3	3	1	5	3	3	1)		- 0.357 682 (93.6%)
	β	26	(7	3	3	1	5	3	3	1)		
C_3^-	α	25	(7	3	3	1	5	2	3	1)		- 0.337 699 (92.2%)
	β	26	(7	3	3	1	5	3	3	1)		
C_4	α	71	(19	7	7	2	20	7	7	2)	Full space	- 0.465 414 (100%)
	β	73	(19	7	7	2	20	8	8	2)		
C_4^-	α	71	(19	7	7	2	20	7	7	2)	Full space	- 0.522 467 (100%)
	β	72	(19	7	7	2	20	7	8	2)		
C_4	α	30	(8	3	3	1	8	3	3	1)		- 0.415 027 (89.2%)
	β	32	(8	3	3	1	8	4	4	1)		
C_4^-	α	30	(8	3	3	1	8	3	3	1)		- 0.464 165 (88.8%)
	β	31	(8	3	3	1	8	3	4	1)		

TABLE VI. MBPT/CC energies C_3/C_3^- and C_4/C_4^- obtained with FOCOs. Energies in atomic units.

	C_3	C_3^-	C_4	C_4^-
SCF	-113.369 150	-113.438 040	-151.203 385	-151.287 139
MBPT(2)	-0.382 223	-0.366 342	-0.465 414	-0.522 467
Calculations with FOCOs				
Number of FOCOs				
α	26	25	30	30
β	26	26	32	31
Correlation energy				
MBPT(2)	-0.357 682	-0.337 699	-0.415 028	-0.464 166
MBPT(3)	-0.366 758	-0.356 603	-0.444 405	-0.479 899
CCSD	-0.376 265	-0.367 960	-0.454 994	-0.488 674
CCSD + T(CCSD)	-0.399 792	-0.383 938	-0.473 438	-0.508 679
E_{corr}^a	-0.424 333	-0.412 581	-0.532 824	-0.566 980
$E_{\text{corr}}^{\text{SC}}^b$	-0.427 222	-0.416 503	-0.530 915	-0.572 571
Largest coupled cluster amplitudes				
T_1	0.038	0.085	0.074	0.078
T_2	-0.101	0.092	-0.081	-0.117

^a Calculated using Eq. (3).^b Calculated using Eqs. (3) and (4a).

mined with all virtual orbitals. The second observation is that this percentage is usually better for the neutral molecule than for the anion, but when the active space becomes more complete, both percentages converge to very similar values.

(v) In the final step, the FOCOs were used to perform the coupled cluster calculations for the neutral and anionic carbon chains. As mentioned before, we chose the CCSD + T(CCSD) implementation of the CC method. For C_5/C_5^- and C_6/C_6^- , the results are presented in Table IV. For C_3/C_3^- and C_4/C_4^- , we considered only one level of the FOCO reduction (see Table V). The CC results for these systems are presented in Table VI. The final value of the correlation energy for each system (entry E_{corr} in the tables) was calculated as

$$E_{\text{corr}} = E_{\text{MBPT}(2)} + E_{\text{h.o.}}, \quad (3)$$

where the higher-order correlation contributions were calculated in two ways defined by the following expressions:

$$E_{\text{h.o.}} = E_{\text{CCSD} + \text{T}(\text{CCSD})}^{\text{FOCO}} - E_{\text{MBPT}(2)}^{\text{FOCO}};$$

$$E_{\text{h.o.}}^{\text{SC}} = \frac{1}{\eta} (E_{\text{CCSD} + \text{T}(\text{CCSD})}^{\text{FOCO}} - E_{\text{MBPT}(2)}^{\text{FOCO}}) \quad (4a)$$

and

$$\eta = E_{\text{MBPT}(2)}^{\text{FOCO}} / E_{\text{MBPT}(2)}. \quad (4b)$$

This gives rise to two entries in Tables IV and VI, E_{corr} and $E_{\text{corr}}^{\text{SC}}$. The scaling factor in the second expression was taken as the ratio of the second-order energy determined with FOCOs $E_{\text{MBPT}(2)}^{\text{FOCO}}$ and the second-order energy calculated with all virtual orbitals $E_{\text{MBPT}(2)}$. Our experience indicates that the above scaling procedure produces an improved estimation of the correlation contribution from higher orders.¹⁹⁻²¹

(vi) The electron affinities were calculated by subtracting the total electronic energies of the neutral system from the anion.

III. RESULTS AND DISCUSSION

The present paper demonstrates an application of the UHF/FOCO/CC technique to study electron affinities of polyatomic molecular clusters. By using the FOCO technique, the computational time is significantly reduced, which makes the CC calculation feasible for larger molecular systems with quality basis sets. Worth mentioning is that the FOCO optimization takes a comparable amount of central processing unit (CPU) time as the SCF calculation, and the Newton-Raphson process converges quite fast, normally somewhat faster for the neutral than for the anion. The algorithms for calculating the gradient and Hessian matrices run considerably faster on a vector machine, such as CONVEX 210 used in the present calculations, due to the clean loop structure. The FOCO optimization requires relatively little disk space because it uses only selected transformed molecular integrals which have two occupied and two virtual indices.

The calculated values of the vertical electron affinities are presented in Table VII and compared with experimental estimates of Smalley *et al.*⁷ In the calculation, we used the values of the higher-order correlation corrections obtained with Eq. 4(b) which includes scaling. Although if the non-

TABLE VII. Comparison of calculated and experimental electron affinities for C_3 , C_4 , C_5 , and C_6 in e.V.

	C_3/C_3^-	C_4/C_4^-	C_5/C_5^-	C_6/C_6^-
Calculated				
SCF	1.87	2.28	2.95	2.62
SCF + $E_{\text{corr}}^{\text{SC}}$	1.58	3.41	2.43	3.69
Experiment ^a	1.95	3.70	2.80	4.10

^a S. Yang, K. J. Taylor, M. J. Craycroft, J. Conceicao, C. L. Pettiette, O. Cheshnovsky, and R. E. Smalley, Chem. Phys. Lett. **144**, 431 (1988).

scaled values [Eq. 4(a)] are used, the resulting electron affinities differ by only a few hundredths of an eV. Upon examining the results, one notices that the theoretical electron affinities exhibit the same trend as the experimental values being significantly larger for even chains than for odd chains. Furthermore, the electron affinity increases with the length of the chain for both even- and odd-numbered clusters. It is interesting that the electron correlation contribution to the electron affinity is positive for the even chains and negative for odd chains. Upon comparing the experiment with the theory, one notices that the calculated values are systematically lower than the UPS results. The calculations, though performed with the state-of-the-art methodology using an extended basis set, could still suffer from various inaccuracies such as basis set incompleteness, approximate inclusion of triple excitations and complete neglect of higher excitations, inadequacy of the single reference CC approach, etc. The last problem does not seem to be a serious one because the size of the largest coupled cluster single and double amplitudes (see Tables IV and VI) does not indicate a significant multireference character of the wave functions for the neutral systems or for the anions. Our numerical experience shows that with CC amplitudes not exceeding 0.1, the CC iteration process converges quite fast. This was the case for all calculations performed in this work. Another source of inaccuracies is the theoretical electron affinity values the molecular geometries used in the calculations. In order to verify this point, we performed calculations for the C_4/C_4^- clusters using the geometry of the C_4^- anion optimized at the MBPT(2) level. The resulting vertical ionization potential was only 0.05 eV different from the vertical electron affinity, despite a noticeable difference in the geometries of C_4 and C_4^- . There is also the possibility that the experimental results suffer from a systematic error, which is not ruled out by Smalley *et al.*⁷ It is clear that more precise calculations, as well as experimental measurements, are needed to eliminate the existing discrepancies.

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