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An examination of *ab initio* results for the helium potential energy curve

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Obtaining a ground state potential energy curve for helium has been the subject of much research involving empirical, semiempirical, and *ab initio* methods. In this work, we examine critically recent *ab initio* potentials proposed for this interaction with respect to their ability to predict certain accurate experimental data. To accomplish this analysis, potentials with a modified HFD-B form were fit to the recent theoretical work of van Duijneveldt and co-workers [Vos, van Lenthe, and van Duijneveldt, J. Chem. Phys. **93**, 643 (1990) and Vos, van Mourik, van Lenthe, and van Duijneveldt (to be published)] and Liu and McLean (LM-2) [J. Chem. Phys. **91**, 2348 (1989)]. A well depth ($\epsilon/k = 10.92$ K) and a separation at the minimum ($r_m = 2.9702$ A) consistent with both determinations were chosen and the properties of helium were calculated based on these potentials. These "mimic" potentials fail to predict the very low temperature ^{4}He and ^{3}He virials and one of them [Vos, van Maurik, van Lenthe, and van Duijneveldt (to be published)] also fails to predict the very accurate room temperature viscosity of Vogel [Ber. Bunsenges. Phys. Chem. **88**, 997 (1984)]. For a potential which was fit as closely as possible to the LM-2 potential at its maximum suggested depth ($\epsilon/k = 10.97$ K), the virials are satisfactorily predicted. This compromise potential appears to be the best characterization of the He–He interaction in its ability to predict a variety of experimental data as well as being consistent with *ab initio* results.

I. INTRODUCTION

In this paper, we analyze critically two recent *ab initio* potentials[1-3] for the helium dimer with respect to their ability to predict certain accurate experimental data. The potentials which were developed using different *ab initio* approaches are in fair agreement. These different approaches are briefly summarized. In order to test the potentials which are available only in numerical form, we found analytical expressions which have a well depth ($\epsilon/k = 10.92$ K) and a separation at the minimum ($r_m = 2.9702$ A) consistent with *both ab initio* potentials and which pass within the stated error bars. We then performed our calculations with these "mimic" potentials. We found that each such function does not predict the lowest temperature virials within experimental error and one does not predict room temperature viscosity. The sign of the deviation from experiment suggests the need for a deeper potential well. We then constructed a potential with a well depth set at the maximum allowed by the error bars associated with one[3] of the *ab initio* potentials and which was as close as possible to it in the rest of the well. This *compromise* potential predicts the low temperature ^{4}He virials within experimental error, and the reference virial at $T = 20.7$ K closer than previous constructions. In the case of ^{3}He, the potential predicts the virials except at the two lowest temperatures where the deviations are only slightly greater than the experimental error. In addition, the viscosity[4] and integral cross section data are also predicted, as they are by other recent potentials.[5,6]

II. *AB INITIO* POTENTIALS

A. IBM potential

Liu and McLean[3] reported that their LM-2 potential was obtained "by careful convergence studies with respect to configuration space, through a sequence of interacting correlated fragment (ICF) wave functions, and with respect to the primitive Slater-type basis used for orbital expansion...The ICF model,[7] applied at a sequence of levels going to higher accuracy, couples the introduction of intra- and interfragment correlations, so that convergence is a function of only a single parameter... ." Initially, they were working from an inadequate primitive basis, which resulted in an underestimation of the well depth. The deeper well of the semiempirical potential of Aziz *et al.*[5] ($\epsilon/k = 10.948$ K), required by recent second virial data, led Liu and McLean to enlarge their primitive basis set resulting in their LM-2 potential. This potential provided to be in very good agreement with the Aziz *et al.* Hartree–Fock dispersion (HFD)-B(HE) potential.[5] Numerical values of the LM-2 potential are given in Table I along with estimated errors.

B. Utrecht potential

Vos, van Lenthe, and van Duijneveldt[1,2] used a multireference single and double configuration-interaction method (MR-SDCI) to calculate the binding energy of the He dimer. By progressively extending the multireference configuration set, they followed the convergence of the binding energy to the configuration-set limit (full CI). They also applied a variant of the Pople size-extensivity correction

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TABLE I. Values of $V(r)$ for some *ab initio* potentials.

r (bohr)	LM-2 (K)	Error (%)	LM-2A (K)	Error (%)	VVVVR (K)	Error (%)
3.0	3767	0.292	3783	0.291	3783	0.238
3.5	1112	0.270	1117	0.269	1117	0.269
4.0	293.1	0.205	295.3	0.203	295.1[a]	0.102
4.3	118.3	0.254	119.4	0.251	119.3	0.168
4.6	39.13	0.486	39.66	0.479	39.64	0.227
4.8	13.52	0.962	13.83	0.940	13.82	0.434
5.0	− 0.33	n/a	− 0.154	n/a	− 0.160[a]	n/a
5.1	− 4.43	1.806	− 4.3	1.860	− 4.3	0.698
5.2	− 7.23	0.830	− 7.14	0.840	− 7.14	0.420
5.4	− 10.18	0.393	− 10.14	0.394	− 10.13	0.197
5.6	− 10.94	0.274	− 10.92	0.275	− 10.919[a]	0.092
5.8	− 10.56	0.284	− 10.56	0.284	− 10.555	0.066
6.0	− 9.64	0.207	− 9.65	0.207	− 9.649	0.052
6.5	− 6.868	0.189	− 6.883	0.189	− 6.883[a]	0.029
7.0	− 4.601	0.130	− 4.614	0.130	− 4.615	0.043
7.5	− 3.057	0.164	− 3.066	0.163	− 3.067	0.065
8.0	− 2.062	0.242	− 2.065	0.242	− 2.065	0.097
8.5	− 1.412	0.212	− 1.415	0.212	− 1.415	0.141
9.0	− 0.985	0.305	− 0.988	0.304	− 0.988	0.202
10.0	− 0.512	0.586	− 0.512	0.586	− 0.512	0.391
12.0	− 0.164	1.892	− 0.164	1.829	− 0.164	1.220

[a] Calculated with the basis set LARSAT and Pople-2 correction within the MR-SDCI framework.

(Pople-2). With a combined atomic orbital basis set (LARGE + SATBF or LARSAT) and a 37-reference configuration set, they obtained values shown in Table I at 4.0, 5.0, 5.6, and 6.5 bohr within the framework of the MR − SDCI method. Vos *et al.*[1] believe that the extrapolation to 100% intraatomic correlation energy used by Liu and McLean[3] in the development of the LM-2 potential is not theoretically justified. They[2] suggest a modified LM-2A potential which is the LM-2 of Liu and McLean *without* extrapolation to 100% intraatomic correlation energy, but with extrapolation *only* to extra dispersion. This extrapolated LM-2A potential agrees quantitatively with the calculated LARSAT points. Numerical values for the LM-2A also appear in Table I with associated errors.

C. Recommended *ab initio* potential (Utrecht)

Vos, van Mourik, van Lenthe, and van Duijneveldt[2] (VVVV) have recommended a nonrelativistic *ab initio* potential (VVVVR) in the Born–Oppenheimer approximation designed to pass through their four calculated LARSAT points. The other points in the range beyond 4.0 bohr are estimated using fits to the LARSAT, LM-2A, and ICF3[3] points at separations of 4.0, 5.0, 5.6, and 6.5 bohr. The additional points at 3.0 and 3.5 bohr were chosen to be equal to the LM-2A values. The recommended potential (the VVVVR) is also shown in Table I. The error bars given reflect the uncertainty due to the remaining incompleteness of the one-electron and N-electron (configuration) basis sets only.

III. MIMIC POTENTIALS

A. Mimic of the Utrecht potential

To mimic the recommended *ab initio* potential of van Duijneveldt and co-workers,[2] we used a piecewise HFD-B[8]

form modified to include individual damping (ID) of the dispersion coefficients for $r \leqslant r_m$. This new form, which we dub HFD-ID is given by

$$V(r) = \epsilon V^*(x), \tag{1}$$

where

$$V^*(x) = A^* \exp(-\alpha^* x + \beta^* x^2) - F_6(x)c_6/x^6$$
$$- F_8(x)c_8/x^8 - F_{10}(x)c_{10}/x^{10}$$
$$- F_{12}(x)c_{12}/x^{12} \tag{2}$$

with

$$F_n(x) = \exp[-(D_n/x - 1)^2], \quad x \leqslant 1 \tag{3}$$

$$F_n(x) = 1, \quad x \geqslant 1 \tag{4}$$

and

$$x = r/r_m. \tag{5}$$

Some of the parameters (found in Table II) differ for $r \leqslant r_m$ and $r \geqslant r_m$. Since the new Utrecht potential and LM-2A potential are very close, this function also represents the LM-2A potential to within its error bars. That the HFD-ID is able to represent either the Utrecht recommended or LM-2A *ab initio* potentials can be gleaned from Tables III and IV.

B. Mimic (i) of the IBM LM-2 potential (LM2M1)

Aziz and Slaman,[6] in an effort to reproduce the second virial coefficients of ⁴He and ³He as well as possible at the lowest measured temperatures, constructed the HFD-B2 potential with a well depth ($\epsilon/k = 10.94$ K) and separation at the minimum ($r_m = 2.97$ Å) close to those of the LM-2. This potential may be regarded as an improvement over the HFD-B(HE) of Aziz *et al.*[5] in that it reproduced the virials somewhat better and is at the same time closer to the LM-2 *ab initio* potential. In fact, the HFD-B2 potential is able to

TABLE II. Parameters for the HFD-ID potential.[a]

Short range $0 < x \leqslant 1.0$

A^*	$1.782\ 988\ 26 \times 10^5$
α^*	$10.237\ 518\ 77$
β^*	$-2.276\ 098\ 71$
β (Å^{-2})	-0.258
D_6	$1.465\ 162\ 5$
D_8	1.2
D_{10}	1.1
D_{12}	1.0
c_{12}	0.0
C_{12} (a.u.)	0.0
σ (Å)	$2.643\ 858$

Long range $1.0 \leqslant x < \infty$

A^*	$2.949\ 923\ 81 \times 10^5$
α^*	$11.296\ 968\ 81$
β^*	$-1.323\ 313\ 21$
β (Å^{-2})	-0.15
c_{12}	$0.038\ 448\ 70$
C_{12} (a.u.)	1300.0

Parameters valid for the entire range $0 < x < \infty$

c_6	$1.351\ 125\ 51$
c_8	$0.414\ 193\ 65$
c_{10}	$0.170\ 979\ 26$
C_6 (a.u.)	1.461
C_8 (a.u.)	14.11
C_{10} (a.u.)	183.5
ϵ/k (K)	10.92
r_m (Å)	$2.970\ 2$

[a] The values for C_6, C_8, C_{10}, C_{12}, D_6, D_8, D_{10}, D_{12}, ϵ/k, r_m, and β are used to define the potential and are not truncated. Not all figures displayed are significant. Some are displayed only to avoid round off errors.

TABLE III. Percentage deviations of the HFD-ID potential from the VVVVR *ab initio* values of van Duijneveldt and co-workers (Refs. 1 and 2).

r (bohr)	VVVVR (K)	Error (%)	Deviation (%) from VVVVR[a] potential HFD-ID[b]	
3.0	3783	0.238	-0.165	Y
3.5	1117	0.269	-0.179	Y
4.0	295.1	0.102	0.002	Y
4.3	119.3	0.168	0.060	Y
4.6	39.64	0.227	-0.052	Y
4.8	13.82	0.434	-0.368	Y
5.0	-0.160	n/a	n/a	n/a
5.1	-4.3	0.698	-0.667	Y
5.2	-7.14	0.420	-0.348	Y
5.4	-10.13	0.197	-0.130	Y
5.6	-10.919	0.092	0.011	Y
5.8	-10.555	0.066	0.054	Y
6.0	-9.649	0.052	0.044	Y
6.5	-6.883	0.029	0.025	Y
7.0	-4.615	0.043	-0.024	Y
7.5	-3.067	0.065	-0.055	Y
8.0	-2.065	0.097	0.090	Y
8.5	-1.415	0.141	0.119	Y
9.0	-0.988	0.202	-0.022	Y
10.0	-0.512	0.391	-0.003	Y
12.0	-0.164	1.220	-1.126	Y

[a] The entry "Y" indicates agreement with the *ab initio* potential, "N" indicates lack of agreement.
[b] Mimic of VVVVR.

TABLE IV. Percentage deviations of the HFD-ID potential from the LM-2A *ab initio* values of van Duijneveldt and co-workers (Refs. 1 and 2).

r (bohr)	LM-2A (K)	Error (%)	Deviation (%) from the LM-2A[a] potential HFD-ID[b]	
3.0	3783	0.291	-0.165	Y
3.5	1117	0.269	-0.179	Y
4.0	295.3	0.203	-0.066	Y
4.3	119.4	0.251	-0.024	Y
4.6	39.66	0.479	-0.103	Y
4.8	13.83	0.940	-0.440	Y
5.0	-0.154	n/a	n/a	n/a
5.1	-4.3	1.860	-0.667	Y
5.2	-7.14	0.840	-0.348	Y
5.4	-10.14	0.394	-0.032	Y
5.6	-10.92	0.275	0.020	Y
5.8	-10.56	0.284	0.102	Y
6.0	-9.65	0.207	0.054	Y
6.5	-6.883	0.189	0.025	Y
7.0	-4.614	0.130	-0.046	Y
7.5	-3.066	0.163	-0.088	Y
8.0	-2.065	0.242	0.090	Y
8.5	-1.415	0.212	0.119	Y
9.0	-0.988	0.304	-0.022	Y
10.0	-0.512	0.586	-0.003	Y
12.0	-0.164	1.829	-1.126	Y

[a] The entry Y indicates agreement with the LM-2A, N indicates lack of agreement.
[b] Mimic of VVVVR.

reproduce all second (Standards Laboratory) virials for ^{4}He and ^{3}He to within experimental error from 1.47 to 623 K. (In this respect, the HFD-B2 could also serve to correlate second virials for possible use in the new International Temperature Scale of 1990 (ITS-90)[9]]. Between 6.0 and 8.0 bohr, the HFD-B2 is somewhat deeper than the LM-2 potential.

By choosing a well depth of 10.92 K and r_m of 2.9702 Å, we have constructed a potential of the HFD-B form in closer agreement with the LM-2 potential than the HFD-B2, which at the same time has energy and length parameters consistent with those of the Utrecht VVVVR as well as the LM-2 potential. Like the HFD-B(HE) and HFD-B2 potentials, it possesses the *ab initio* dispersion coefficients of Thakkar[10] and Koide *et al.*[11] Its wall was constructed to fit the room temperature viscosity of Vogel[4] and the Green's-function Monte Carlo (GFMC) determination of the Born–Oppenheimer interaction energy at 1.0 bohr by Ceperley and Partridge.[12]

This new potential is still deeper than the LM-2 potential in the more limited region between 6.5 and 8.0 bohr. One can modify this potential in the region between 6.5 and 8.0 bohr by an "add on," so that the whole modified potential (LM2M1) lies within the error bars of the LM-2 (see Appendix A for a description of the add-on potential used). The parameters for the LM2M1 potential are found in Table V. Table VI shows how closely the LM2M1 potential agrees with the LM-2 *ab initio* potential. By including the add on, one reduces the area of the bowl sufficiently to remove the agreement with experiment at the lowest temperature for both the ^{3}He and ^{4}He virials. As noted below, however, the

TABLE V. Parameters for LM2M1 and LM2M2 potentials.[a,b]

	HFD-B base potentials	
	LM2M1	LM2M2
A^*	$1.912\ 871\ 72 \times 10^5$	$1.896\ 353\ 53 \times 10^5$
α^*	10.704 669 80	10.702 035 39
c_6	1.351 125 51	1.346 870 65
c_8	0.414 193 65	0.413 083 98
c_{10}	0.170 979 26	0.170 601 59
C_6 (a.u.)	1.461	1.461
C_8 (a.u.)	14.11	14.11
C_{10} (a.u.)	183.5	183.5
β^*	$-1.933\ 095\ 93$	$-1.907\ 406\ 49$
β (Å^{-2})	$-0.219\ 12$	$-0.216\ 31$
D	1.421 4	1.408 8
ϵ/k (K)	10.92	10.97
r_m (Å)	2.970 2	2.969 5
σ (Å)	2.642 331 2	2.641 727 8
	Add-on portions	
A_a	0.001 519 099 2	0.002 600 000 0
x_1	1.003 299 441 1	1.003 535 949 0
x_2	1.508 315 938 3	1.454 790 369 0

[a] The values for C_6, C_8, C_{10}, β, ϵ/k, r_m, and D are used to define the base potentials and are not truncated. Not all figures displayed are significant. Some are displayed only to avoid round-off errors.

[b] The form of the HFD-B portion of the potential can be found from Aziz and co-workers (Refs. 5, 6, and 8). The form of the add on can be found in the Appendix.

LM2M1 potential is in closer agreement with these virials than the HFD-ID.

C. Mimic (ii) of the IBM LM-2 potential (LM2M2)—the compromise potential

Following the procedure indicated above, a deeper mimic potential with add on (LM2M2) was constructed. For this potential, the well depth is 10.97 K, which is the upper limit for the LM-2 potential. The parameters for the LM2M2 potential are also presented in Table V. With the deeper well, it does not seem possible to construct a potential which would lie within all the error bars. Within the well, the compromise potential exceeds errors associated with the LM-2 potential by only 0.13% at 6.0 bohr and 0.07% at 7.0 bohr. It can be seen in Table VI how closely this potential agrees with the LM-2 *ab initio* potential and in Table VII how well it agrees with the GFMC determination of the Born–Oppenheimer interaction energy of Ceperley and Partridge.[12]

IV. RESULTS AND DISCUSSION

Second virial coefficients for ^3He and ^4He and the viscosity and thermal conductivity of ^4He were calculated on the basis of the HFD-ID, LM2M1, and LM2M2 potentials. The second virials sense the depth and the area of the well, while the viscosity senses the position of the lower repulsive wall of the potential. Results are presented in Tables VIII and IX. It is seen that the HFD-ID potential predicts *neither* the lowest temperature virials *nor* the accurate viscosity value at room temperature. However, like the HFD-B2, the

TABLE VI. Percentage deviations of LM2M1 and LM2M2 "mimic" potentials from the LM-2 *ab initio* values of Liu and McLean (Ref. 3).

			Deviation from the LM-2[a] potential			
r (bohr)	LM-2 (K)	Error (%)	LM2M1 (%)		LM2M2 (%)	
3.0	3767	0.292	0.659	N	0.653	N
3.5	1112	0.270	0.269	Y	0.269	Y
4.0	293.1	0.205	-0.075	Y	-0.057	Y
4.3	118.3	0.254	-0.253	Y	-0.243	Y
4.6	39.13	0.486	-0.357	Y	-0.433	Y
4.8	13.52	0.962	-0.532	Y	-0.884	Y
5.0	-0.33	n/a	n/a	n/a	n/a	n/a
5.1	-4.43	1.806	0.364	Y	-0.965	Y
5.2	-7.23	0.830	0.242	Y	-0.577	Y
5.4	-10.18	0.393	0.270	Y	-0.284	Y
5.6	-10.94	0.274	0.203	Y	-0.258	Y
5.8	-10.56	0.284	0.110	Y	-0.285	Y
6.0	-9.64	0.207	-0.030	Y	-0.335	N
6.5	-6.868	0.189	-0.126	Y	-0.078	Y
7.0	-4.601	0.130	-0.129	Y	0.204	N
7.5	-3.057	0.164	-0.135	Y	-0.030	Y
8.0	-2.062	0.242	0.019	Y	-0.238	Y
8.5	-1.412	0.212	-0.136	Y	-0.128	Y
9.0	-0.985	0.305	-0.276	Y	-0.273	Y
10.0	-0.512	0.586	0.064	Y	0.065	Y
12.0	-0.164	1.829	-1.098	Y	-1.098	Y

[a] The entry Y indicates agreement with the LM-2, N indicates lack of agreement.

LM2M2 potential is able to predict all the ^4He virials[14–18] within experimental error. Interestingly, the deeper well depth brings the prediction of the *reference* virial at $T = 20.7$ K closer to its central value. The predictions of the ^3He virials at $T = 1.47$ and 1.5 K by the LM2M2 potential exceed the experimental error bar by less than 0.1 ml mol^{-1}. Unlike the HFD-ID potential, the LM2M2 potential is able to predict the room temperature viscosity value of Vogel within experimental error. The percentage deviation for the HFD-ID potential at $T = 298.15$ K is -0.24% which is more than twice the experimental error. The sign of the deviation suggests strongly that the recommended *ab initio* potential (Utrecht VVVVA) is too repulsive and the wall of the LM-2 potential is correct.

TABLE VII. Percentage deviations of LM2M2 potential from the *smoothed* theoretical values of Ceperley and Partridge.[a]

r (bohr)	CP (K)	Error (%)	Deviation of LM2M2 from CP[a]	Agreement with CP[a,b]
1.00	2.9193×10^5	0.41	-0.39%	Y
1.25	1.7489×10^5	0.69	-0.25%	Y
1.50	1.0440×10^5	0.77	-0.49%	Y
1.75	6.1646×10^4	0.97	-0.42%	Y
2.00	3.6001×10^4	0.83	-0.02%	Y
2.25	2.0813×10^4	0.96	0.46%	Y
2.50	1.1921×10^4	1.85	0.71%	Y
2.8346	5.5770×10^3	2.87	0.24%	Y
3.00	3.8090×10^3	5.25	-0.46%	Y

[a] Reference 12.
[b] The entry Y denotes agreement between the LM2M2 and the potential of Ceperley and Partridge.

TABLE VIII. Primary second virial data predicted by various potentials.

	Temperature (K)	$B(T)_{\text{expt}}$ (ml mol^{-1})	Error (ml mol^{-1})	Deviation from experiment (ml mol^{-1})		
				HFD-ID[a]	LM2M1[b]	LM2M2[c]
Matacotta *et al.* (Refs. 13 and 14)	1.47	− 173.58	± 0.5	2.03	1.49	0.59
(^{3}He)	1.50	− 170.54	± 0.5	1.95	1.44	0.54
	1.55	− 165.68	± 0.5	1.82	1.39	0.46
	1.73	− 149.99	± 0.4	1.49	1.19	0.27
	1.90	− 137.37	± 0.4	1.29	1.05	0.18
	2.20	− 119.12	± 0.5	1.09	0.90	0.12
	3.00	− 86.31	± 0.5	0.89	0.69	0.18
	4.30	− 57.15	± 0.4	0.70	0.50	0.20
	9.00	− 19.75	± 0.3	0.36	0.23	0.10
	13.80	− 7.33	± 0.2	0.30	0.22	0.13
	20.30	+ 0.24	± 0.2	0.27	0.22	0.14
Berry (Ref. 15)	2.601	− 142.5	± 1.0	1.60	1.27	0.95
(^{4}He)	2.748	− 133.2	± 0.7	1.15	0.84	0.54
	3.330	− 105.8	± 0.7	0.65	0.40	0.17
	4.220	− 79.5	± 0.5	0.64	0.45	0.27
	7.199	− 39.0	± 0.7	0.32	0.21	0.11
	13.804	− 11.7	± 0.4	0.09	0.02	− 0.04
	20.271	− 2.4	± 0.2	0.09	0.03	− 0.01
	27.098	+ 2.5	± 0.3	0.09	0.04	0.00
Kemp *et al.* (Ref. 16)[d]	27.097	2.539	± 0.23	0.05	− 0.00	− 0.04
(^{4}He)	43.794	7.800	± 0.24	0.06	0.01	− 0.01
	54.358	9.306	± 0.23	0.07	0.03	0.01
	63.150	10.111	± 0.24	0.08	0.04	0.02
	83.804	11.198	± 0.24	0.10	0.06	0.04
	172.011	12.186	± 0.25	0.06	0.02	0.02
Gammon (Ref. 17)	98.15	11.522	± 0.05	0.18	0.14	0.13
(^{4}He)	123.15	11.984	± 0.05	0.08	0.05	0.04
	148.15	12.174	± 0.05	0.04	0.00	− 0.00
	173.15	12.228	± 0.05	0.02	− 0.02	− 0.02
	198.15	12.209	± 0.05	0.01	− 0.03	− 0.03
	223.15	12.018	± 0.05	0.00	− 0.03	− 0.04
	248.15	12.065	± 0.05	− 0.00	− 0.03	− 0.04
	273.15	11.968	± 0.05	0.00	− 0.03	− 0.03
	298.15	11.863	± 0.05	0.00	− 0.03	− 0.03
	323.15	11.765	± 0.05	0.00	− 0.02	− 0.02
	348.15	11.647	± 0.05	0.01	− 0.02	− 0.02
	373.15	11.539	± 0.05	0.01	− 0.02	− 0.02
	398.15	11.433	± 0.05	0.01	− 0.02	− 0.02
	423.15	11.329	± 0.05	0.01	− 0.01	− 0.02
Kell *et al.* (Ref. 18)	298.15	11.83	± 0.03	0.04	0.01	0.00
(^{4}He)	623.15	10.61	± 0.01	− 0.01	− 0.03	− 0.03

[a] Mimic of VVVVR (ϵ/k = 10.92 K).
[b] Mimic of LM-2 (ϵ/k = 10.92 K).
[c] Mimic of LM-2 (ϵ/k = 10.97 K).
[d] Smoothed National Measurement Laboratory (NML) values.

V. CONCLUSIONS

The *ab initio* potentials VVVVR (ϵ/k = 10.92 K) and LM2M1 mimic with well depth set at the same value are in fairly close agreement. Our tests on the ability of *ab initio* potentials to predict low temperature virials and room temperature viscosity demonstrate that, in these respects, the LM2M1 potential appears to be superior to the Utrecht recommended potential. However, the LM2M2 mimic potential with its well depth set at the maximum depth of the LM-2 *ab initio* potential, viz., ϵ/k = 10.97 K, predicts values closest to the low temperature virials of Berry[15] and Mata-

cotta *et al.*[14] In addition, the prediction of the room temperature viscosity is just within experimental error.

For these reasons, the LM2M2 version of the LM-2 appears to be most consistent with experiment and is perhaps the best characterization of the He–He interaction in spite of the small discrepancies at atom separations at 6.0 and 7.0 bohr between it and the *ab initio* LM-2 potential. The maximum deviation is − 0.33% which occurs at 6.0 bohr, where the error bars are ± 0.21%.

For completeness, we have found that the current LM2M2 potential predicts the integral cross sections[27,28] almost as well as the HFD-B(HE) potential of Aziz *et al.*[5]

TABLE IX. Primary transport data predicted by various potentials.

	Temperature range (K)	Error bars (%)	Maximum ± deviation (%)		
			HFD-ID[a]	LM2M1[b]	LM2M2[c]
Viscosity ^{4}He					
Vogel (Ref. 4)	298	± 0.1%	− 0.24	− 0.14	− 0.15
Vogel (Ref. 4)	298–623	± 0.1–0.3%	− 0.27	− 0.18	− 0.18
Vogel (Ref. 19)[d]	298–641	± 0.3%	− 0.25	− 0.15	− 0.11
Clarke/Smith (Ref. 20)[e]	77–374	± 1%	− 1.11	− 0.94	− 0.95
Clarke/Smith (Ref. 20)[e,f]	120–360	± 1%	− 1.34	− 1.19	− 1.18
Guevara et al. (Ref. 21)[e]	1100–1800	± 0.6%	− 0.62	− 0.62	− 0.62
Guevara et al. (Ref. 21)[e]	1100–2150	± 0.6%	3.80	3.71	3.71
Kestin et al. (Ref. 22)	300.65	± 0.3%	− 0.31	− 0.21	− 0.21
Thermal conductivity ^{4}He					
Assael et al. (Ref. 23)	308.15	± 0.2%	− 0.07	0.03	0.03
Kestin et al. (Ref. 22)	300.65	± 0.3%	− 0.13	− 0.03	− 0.04
Acton/Kellner (Ref. 24)	4–20	± 1.1%	− 1.34	− 1.26	− 1.24
Acton/Kellner (Ref. 24)[f]	4–20	± 1.1%	− 1.10	− 1.04	− 1.03
Haarman (Ref. 25)	328–468	± 0.3%[h]	0.28	0.37	0.36
Jody et al. (Ref. 26)	400–2500	± 4.7%	4.63	4.71	4.71

[a] Mimic of VVVVR ($\epsilon/k = 10.92$ K).
[b] Mimic of LM-2 ($\epsilon/k = 10.92$ K).
[c] Mimic of LM-2 ($\epsilon/k = 10.97$ K).
[d] Data obtained with edge-correction C.
[e] These capillary flow relative viscosity results have been renormalized using the accurate value (error ± 0.1%) near room temperature of Vogel (Ref. 4).
[f] Smoothed.
[g] Error of ± 0.1% at 298 K, increasing to ± 0.3% at 623 K.
[h] The estimated error is considered (Ref. 22) to be larger than this because the hot wire did not remain centrally located during operation.

and certainly better than the HFIMD (average) potential of Feltgen et al.[27]

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APPENDIX A

The form of the LM2M1 and LM2M2 potentials is that of the usual HFD-B form with a versatile new empirical add-on functional form attached to it. This add-on function can be used in conjunction with any existing form to enhance its predictive ability while at the same time introducing a minimal number of additional parameters. The form is mathematically simple and can be easily adjusted when fitting it to experimental data. This form is smoothly added to an existing potential to create a new potential with additional flexibility while retaining relative simplicity of form. It can be easily combined with any existing potential form at precisely the location where that form may be too inflexible to fit the relevant data. In this way, the potential can be adjusted in one region without distorting it elsewhere. When the "add-on" function $V_a(r)$ is added to the "base" potential $V_b(r)$, the form of the resulting interatomic potential becomes

$$V(r) = V_a(r) + V_b(r), \quad\quad (A1)$$

which can be alternatively expressed as

$$V(r) = \epsilon[V_a^*(x) + V_b^*(x)], \quad\quad (A2)$$

where $V_{(x)}^{*a}$ represents the present add-on potential in *reduced* form and $V_b^*(x)$ represents the *reduced* base potential to which it is added (in this case, the HFD-B3) to give the total potential $V(r)$. The reduced form of the add-on part is

$$V_a^*(x) = A_a\{\sin[B(x - x_1) - \pi/2] + 1\}, \quad x_1 \leqslant x \leqslant x_2$$

$$= 0, \quad x < x_1 \text{ or } x > x_2, \quad\quad (A3)$$

where $x = r/r_m$ and $B = 2\pi/(x_2 - x_1)$. The adjustable parameters are x_1, and x_2, and A_a, and the values used for ϵ/k and r_m are simply those of the base potential. Since the slope of the curve in Eq. (A3) is zero at x_1 and x_2, there is no discontinuity introduced in the derivative of $V(r)$ at the points where $V_a(r)$ is added onto $V_b(r)$. The parameters of the add-on potential for the LM2M1 and LM2M2 potentials can be found in Table V along with the parameters for the base HFD-B potential, the form of which may be found from Aziz and co-workers.[5,6,8]

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