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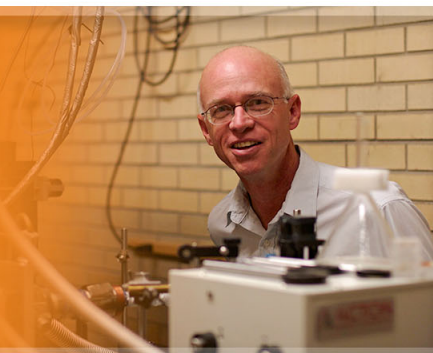
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Examination of the correlation energy and second virial coefficients from accurate *ab initio* calculations of rare-gas dimers

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Calculations of rare-gas dimers (He–He, Ne–Ne, Ar–Ar, He–Ne, He–Ar, and Ne–Ar) at the coupled-cluster single double (triple) level of theory with large basis sets including bond functions and counterpoise corrections are reported over a wide range of 100 internuclear separations. These results are compared to experimental curves obtained from fitting to rovibrational spectra, and to second virial coefficients and Boyle temperatures. Accurate analytic potentials are developed for the total interaction energy, Hartree–Fock (exchange) energy, and correlation (dispersion) energy; the transferability of the latter is demonstrated to very high accuracy even in the region of considerable wave function overlap. These calculations represent an important set of benchmarks that can be used to develop improved empirical molecular mechanical force fields and new quantum models.

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I. INTRODUCTION

One of the main challenges in force field development involves the accurate modeling of intermolecular forces.^{1,2} Two-body energies play a key role in these interactions, and consequently are important to study using quantum chemistry. Unlike strong covalent, ionic, or polar interactions, the relatively weak dispersion interactions of van der Waals complexes often are more challenging to obtain from quantum mechanical calculations since binding arises mainly from electron correlation.³ Dispersion interactions have a cumulative effect in condensed-phase systems, and consequently are very important in molecular simulations since they play a significant role in the determination of the internal pressure and cohesive energy, and the modeling of hydrophobic effects. The proper treatment of long-range dispersion interactions has traditionally been either absent from or problematic for density-functional theory and semiempirical quantum models; rare gases are an important benchmark system to characterize with higher level methods.

In this article, high-level *ab initio* calculations of rare-gas dimers are presented. The goals of this work are (1) to report accurate potential energy curves (including the Hartree–Fock and correlation energy components) for rare-gas dimers over a large range of internuclear separations, (2) to address how well quantum chemical calculations at this level can reproduce experimental quantities derived from the two-body interaction, and (3) to investigate the transferability of the correlation energy in these systems. The present work represents a systematic study of rare gases at very high basis set levels, with dense sampling (100 points) over a large range of internuclear distances that extends previous work reported by Cybulski *et al.*⁴ It is the hope that these results will serve as important benchmark calculations for the design of new quantum methods (such as semiempirical, density-functional, and multilevel quantum models) that

model electron correlation with increased accuracy and that can be extended to much larger systems.⁵

II. METHODS

A. Quantum calculations

Quantum chemical calculations were performed using MOLPRO 2000⁶ at the coupled-cluster single double (triple) [CCSD(T)] level of theory using a singly augmented correlation consistent basis set (aug-cc-pV5Z)⁷ with a set of *3s3p2d2f1g* bond functions⁴ and using counterpoise corrections.⁸

A set of 100 radial points were generated for each rare-gas dimer from the empirical equation,

$$r_{\alpha i} = R_{eq}(\alpha) \cdot [1 + \text{sign}(\Delta_{\alpha} + i - 1) \cdot \gamma \times (\Delta_{\alpha} + i - 1)^2],$$
$$i = 1 \cdots 100, \quad (1)$$

where “ α ” is an index that indicates the particular dimer, $R_{eq}(\alpha)$ is the radial distance of the minimum on the high-level reference potential energy curve for the “ α ” dimer, $r_{\alpha i}$ is the i th radial sample point, Δ_{α} is an integer shift function given by $\Delta_{\alpha} = -\text{INT}[60/\sqrt{R_{eq}(\alpha)}]$, and γ is a unitless parameter ($\gamma = 0.00036$ for all the curves in the present work). Equation (1) provides a dense set of sampling points for each dimer that spans a broad range of internuclear separations from fairly high up on the repulsive wall to well out into the attractive tail region, and allows a higher concentration of points centered around $R_{eq}(\alpha)$.

B. Analytic potential functions

The 100 calculated radial points provide a reliable benchmark data set from which analytic functional forms for the Hartree–Fock, correlation, and total potential can be derived. For this purpose a nonlinear weighted least-squared fitting procedure was adapted and a number of functional forms were tested. In the end, several of the forms could fit the data to very high accuracy (five decimal places or better

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TABLE I. Parameters for analytic interaction potential $V(r)$, Hartree–Fock exchange potential $V_{\text{HF}}(r)$, and correlation potential $V_C(r)$ curves.^a

Parameter	He–He	Ne–Ne	Ar–Ar	HeNe	HeAr	NeAr
$G_{11} (E_h)$	6.2154×10^{-4}	-3.2048×10^{-4}	2.1887×10^{-4}	-8.7287×10^{-3}	5.5565×10^{-2}	5.1911×10^{-4}
$G_{21} (a_0^{-1})$	0.208 10	0.821 72	0.131 89	0.263 92	8.3824×10^{-2}	0.228 22
$G_{31} (a_0)$	0.881 71	3.2949	3.2042	0.775 03	-3.1381	3.0094
$G_{12} (E_h)$	1.5583×10^{-4}	-2.7712×10^{-3}	-1.4886×10^{-2}	-0.140 62	8.1665×10^{-4}	7.9007×10^{-3}
$G_{22} (a_0^{-1})$	1.5421	1.1097	0.460 24	0.566 50	0.791 37	0.502 42
$G_{32} (a_0)$	2.7637	2.2072	1.7768	0.467 47	2.6529	1.7699
$A (E_h)$	6.620 02	88.5513	82.9493	24.4219	23.1693	75.4390
$\alpha (a_0^{-1})$	1.885 53	2.206 26	1.454 85	2.057 66	1.633 29	1.749 39
$\beta (a_0^{-2})$	-0.063 981 9	-0.024 985 1	-0.037 992 9	-0.032 344 3	-0.046 200 8	-0.036 771 5
$b (a_0^{-1})$	1.858 22	1.851 66	1.623 65	2.656 28	1.637 19	1.630 79
$C_6 (E_h a_0^6)$	1.460 98	6.281 74	63.7520	3.052 39	9.387 01	19.0098
$C_8 (E_h a_0^8)$	14.1179	90.0503	1556.46	31.6787	165.522	392.861
$C_{10} (E_h a_0^{10})$	183.691	1679.45	$4.943 79 \times 10^4$	427.732	3797.16	$1.056 27 \times 10^4$
$C_{12} (E_h a_0^{12})$	$3.265 27 \times 10^3$	$4.189 67 \times 10^4$	$2.072 89 \times 10^6$	7725.16	$1.165 18 \times 10^5$	$3.798 79 \times 10^5$
$C_{14} (E_h a_0^{14})$	$7.643 99 \times 10^4$	$1.362 98 \times 10^6$	$1.105 297 \times 10^8$	$1.819 45 \times 10^5$	$4.662 58 \times 10^6$	$1.781 60 \times 10^7$
$C_{16} (E_h a_0^{16})$	$2.274 72 \times 10^6$	$5.629 06 \times 10^7$	$7.247 72 \times 10^9$	$5.440 12 \times 10^6$	$2.368 61 \times 10^8$	$1.060 75 \times 10^9$

^aValues for the parameters A , α , β , b , and C_6 – C_{16} were taken from Ref. 4.

in the binding energy). For consistency with other work, the analytic form of the *total* binding energy curves was taken to be that used by Korona *et al.*⁹ for the helium dimer, and later used by Cybulski and Toczylowski⁴ for rare-gas dimers. For the total interaction potential, the parameters reported by Cybulski⁴ fit very well (as did several other parameter sets), and consequently, to avoid redundancy, their values are adopted here. However, in order to obtain simultaneously an accurate representation for the individual Hartree–Fock exchange $V_{\text{HF}}(r)$ and correlation $V_C(r)$ contributions, additional short ranged terms were required. An excellent fit to $V(r)$, $V_{\text{HF}}(r)$, and $V_C(r)$ could be obtained by the forms:

$$V(r) = V_{\text{HF}}(r) + V_C(r), \quad (2)$$

where

$$V_{\text{HF}}(r) = A e^{-(\alpha R + \beta^2 R^2)} + \sum_{i=1}^2 G_{1i} e^{-G_{2i}(R - G_{3i})^2} \quad (3)$$

and

$$V_C(r) = - \left(\sum_{i=1}^2 G_{1i} e^{-G_{2i}(R - G_{3i})^2} + \sum_{n=3}^8 S_{2n}(R, b) \frac{C_{2n}}{R^{2n}} \right), \quad (4)$$

where the function $S_{2n}(R, b)$ above is a type of switching function¹⁰

$$S_{2n}(R, b) = 1 - e^{-bR} \sum_{k=0}^{2n} \frac{(bR)^k}{k!}, \quad (5)$$

where α , β , A , b , and C_{2n} are the parameters for the total binding energy curve $V(r)$,⁴ and two Gaussian functions characterized by the parameters G_{ij} were added to the repulsive term in Eq. (2) to give $V_{\text{HF}}(r)$ and subtracted from the attractive term in Eq. (2) to give $V_C(r)$. The Gaussian functions were chosen to be of similar form to the empirical core-core corrections terms used in semiempirical calculations.^{11,12} In this way, for example, the correlation contribution might be easily added to semiempirical models as simple one-body terms since it has been demonstrated here for the rare gases that the correlation energy for hetero-

nuclear dimers can be derived from the corresponding homodimer correlation energies. The values of the parameters in Eqs. (2)–(5) are given in Table I.

C. Second virial coefficients and Boyle temperatures

Virial coefficients are derived from the virial equation of state in the grand canonical ensemble, and used to expand the pressure p as a power series in the density ρ as¹³

$$\frac{p}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 \dots, \quad (6)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and $B_j(T)$ is the j th virial coefficient. The second virial coefficient, $B_2(T)$, is a property of the two-body interaction, and a focus of later discussion. In the classical limit, the second virial coefficient for an n -component mixture of monatomic gas particles can be calculated as

$$B_2(T) = \sum_{i=1}^n \sum_{j=1}^n B_{ij}(T) x_i x_j, \quad (7)$$

where x_i is the mole fraction of component i , and $B_{ij}(T)$ is defined by

$$B_{ij}(T) = - \frac{1}{2} \int_0^\infty f_{ij}(r; T) 4\pi r^2 dr + B_{ij}^{\text{QC}}(T), \quad (8)$$

where $f_{ij}(r; T)$ is the Mayer f -function for the ij particle pair, defined as

$$f_{ij}(r; T) = e^{-V_{ij}(r)/k_B T} - 1 \quad (9)$$

and $V_{ij}(r)$ is the classical Born–Oppenheimer two-body pair potential between particles i and j . In Eq. (8), $B_{ij}^{\text{QC}}(T)$ is a quantum correction to the classical second virial coefficient. Quantum corrections, most important for very light particles at low temperatures, can be derived by expansion of the canonical partition function in a power series in Planck's constant h .¹³ Only the h^2 term is considered here in the expression for $B_{ij}^{\text{QC}}(T)$:

$$B_{ij}^{\text{QC}}(T) = \frac{h^2}{24\pi\mu_{ij}(kT)^3} \int_0^\infty e^{-\beta V_{ij}(r)} \left(\frac{dV_{ij}(r)}{dr} \right)^2 r^2 dr, \quad (10)$$

where μ_{ij} is the reduced mass of atoms i and j . The Boyle temperature (T^*) for a gaseous mixture is defined as the temperature for which the second virial coefficient vanishes, and is a quantity easily measured experimentally.

In this work, the two-body pair potentials $V_{ij}(r)$ calculated from high-level electronic structure calculations and fit to analytic forms are used to calculate the second virial coefficients $B_2(T)$ and Boyle temperatures T^* for rare-gas mixtures according to Eqs. (7)–(10).

III. RESULTS AND DISCUSSION

The van der Waals interactions between rare-gas atoms have been studied extensively with *ab initio* methods.^{4,14–20} Accurate calculations of van der Waals interactions^{21–23} require high-level quantum models and very large basis sets (with careful attention paid to basis-set superposition errors)²⁴ to achieve both convergence and high accuracy (Fig. 1). Calculations at the CCSD(T) level of theory using a large augmented correlation consistent basis (aug-cc-pV5Z)^{7,19} supplemented with a set of (3s3p2d2f1g) bond functions,^{25–27} and using a counterpoise correction scheme^{8,28} lead to excellent agreement with the experimental binding curves of Ogilvie and Wang^{29,30} (Fig. 2). This level of theory and basis set has been shown previously to be highly accurate for van der Waals dimers.^{4,19} Table II compares the calculated and experimental equilibrium distance (R_e), well depth (D_e), and frequency (ω_e) for each of the dimers. The calculated results agree closely with the experimental values. The largest error for R_e , D_e , and ω_e is 0.022 Å (Ar–Ar), 0.008 kcal/mol (Ar–Ar), and 0.9 cm^{-1} (He–Ne/He–Ar), respectively.

The temperature-dependent second virial coefficient, $B_2(T)$, is a property derivable from the two-body potential that has been measured experimentally for single-component and binary rare-gas mixtures over a range of temperatures.³¹ Overall, the agreement between the theoretical and experimental second virials is reasonably close (Fig. 3); however, the theoretical curves at this level slightly overestimate the experimental values. The largest errors, not surprisingly, occur for He–He at very low temperatures, where in fact, the second virial coefficients should be computed fully quantum mechanically instead of including quantum effects as a perturbative correction.¹³ The He–He van der Waals potential is notoriously difficult and has been the topic of numerous investigations.^{9,24,32–41} It is the purpose here to assess how well a high-level *ab initio* potential energy curve can reproduce experimental second virial coefficients without recourse to empirical adjustment.⁴² The overall percent error for $B_2(T)$ is around 4%–5% with the exception of He–Ne (11.8%), the lightest dimer with the lowest Boyle temperature that could be computed (see Fig. 3).

A key feature derivable from these calculations is the contribution of the correlation energy to the rare-gas binding energy curves. [The correlation energy for a given basis set is defined to be the difference between the energy of the full

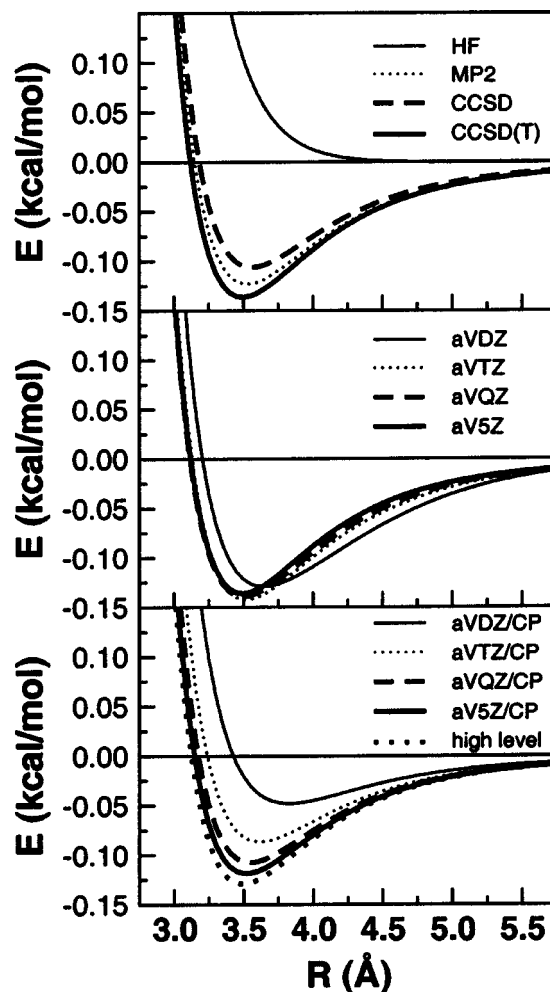


FIG. 1. Potential (binding) energy curves $V(R)$ for Ne–Ar dimer: (1) comparison of different levels of theory using the aV5Z basis (top), (2) comparison of basis sets at the CCSD(T) level of theory (middle), and (3) comparison of basis sets with counterpoise corrections at the CCSD(T) level of theory (bottom).

configuration interaction (CI) solution and the single-reference restricted Hartree–Fock (RHF) solution. In this work, the approximate correlation energy is defined as the difference between the CCSD(T) and HF energies.] The total CCSD(T) binding energy, HF energy, and approximate correlation energy are shown for homonuclear and heteronuclear rare-gas dimers in Fig. 2. The exact correlation energy by definition is always less than or equal to zero. The Hartree–Fock curves are unbound. In molecular simulations, typically a set of empirical combining rules^{43,44} are used to determine the two-body potential energy curves for rare-gas dimers, the most frequently employed is the Lorentz–Berthelot combining scheme for the Lennard–Jones “6–12” potential.⁴³ However, these rules are not always transferable to the heteronuclear rare-gas dimers⁴⁰ mainly since the Hartree–Fock exchange interactions are not simply transferable. However, a simple geometric mean rule can be applied to estimate the correlation potential via

$$\tilde{V}_{C(a,b)}(r) = -\sqrt{|V_{C(a,a)}(r)| \cdot |V_{C(b,b)}(r)|} \approx V_{C(a,b)}(r), \quad (11)$$

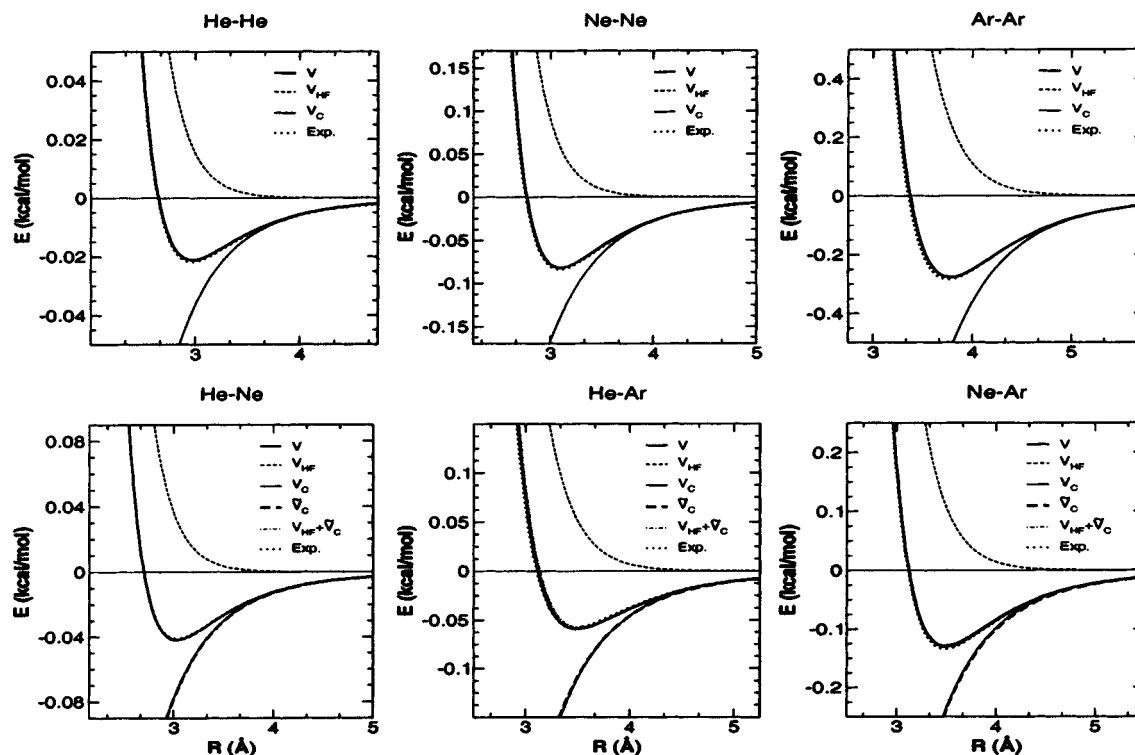


FIG. 2. Comparison of the experimental (Exp) binding energy curves of Refs. 30 and 29 with the calculated CCSD(T) binding energy curves (V), including the separate Hartree-Fock (V_{HF}) and correlation energy (V_C) components. Also shown for the heteronuclear dimers are the approximate correlation energies obtained from the corresponding homodimer curves using a simple geometrical mean combining rule (\tilde{V}_C). The resulting potential energy from the correlation energy (\tilde{V}_C) and the Hartree-Fock (V_{HF}) energy is shown as ($V_{\text{HF}} + \tilde{V}_C$).

where $\tilde{V}_{C(a,b)}(r)$ and $V_{C(a,b)}(r)$ are the estimated and exact correlation energy of the $a-b$ dimer, respectively. For the rare-gas systems studied here, the estimated $\tilde{V}_{C(a,b)}(r)$ is shown to be very accurately *transferable* (Fig. 2). This is consistent with the London formula for the dispersion energy and Slater-Kirkwood approximation;⁴⁴ however, it is of interest that a simple combining rule agrees well even in the

case of He-Ar (where He and Ar have considerably different ionization potentials and atomic polarizabilities). Alternate combining rules of dispersion interactions exist and may be more appropriate for other systems.⁴⁵⁻⁴⁷ However, this article demonstrates explicitly through *ab initio* calculations of the correlation potential that a simple combining rule is transferable between rare-gas atoms. A similar combining rule for C_6 coefficients has been examined in the past^{45,46} and found to be a reasonable approximation for rare-gas interactions; however, it does poorly for rare-gas and alkali

TABLE II. Comparison of the calculated (bold) and experimental (italics) binding energy curves for rare-gas dimers.^a

Dimer	R_e	D_e	ω_e	$B_2(T=300)$	T_B
He-He	2.977	0.021	32.7	12.20	
	<i>2.970</i>	<i>0.022</i>	<i>33.1</i>	<i>11.77</i>	
Ne-Ne	3.099	0.082	29.0	11.93	109.60
	<i>3.091</i>	<i>0.084</i>	<i>28.4</i>	<i>11.16</i>	<i>115.39</i>
Ar-Ar	3.779	0.277	30.3	-13.37	394.70
	<i>3.757</i>	<i>0.285</i>	<i>30.8</i>	<i>-16.40</i>	<i>416.49</i>
He-Ne	3.030	0.042	35.7	12.51	68.63
	<i>3.031</i>	<i>0.041</i>	<i>34.8</i>	<i>12.07</i>	<i>77.82</i>
He-Ar	3.494	0.059	35.6	9.24	198.73
	<i>3.480</i>	<i>0.057</i>	<i>34.7</i>	<i>7.51</i>	<i>207.57</i>
Ne-Ar	3.495	0.129	27.3	5.50	245.39
	<i>3.489</i>	<i>0.134</i>	<i>28.1</i>	<i>4.38</i>	<i>256.43</i>

^aComparison of calculated and experimental values for the equilibrium (minimum energy) distance R_e (Å), dissociation energy D_e (kcal/mol), vibrational wave number ω_e (cm^{-1}), second virial coefficient at 300 K $B_2(T=300)$ (m^3/mol), and Boyle temperature T_B (K). Experimental values for R_e , D_e , and ω_e were taken from Ref. 29 for homodimers and Ref. 30 for heterodimers. Experimental values for $B_2(T=300)$ and T_B were taken from Ref. 31.

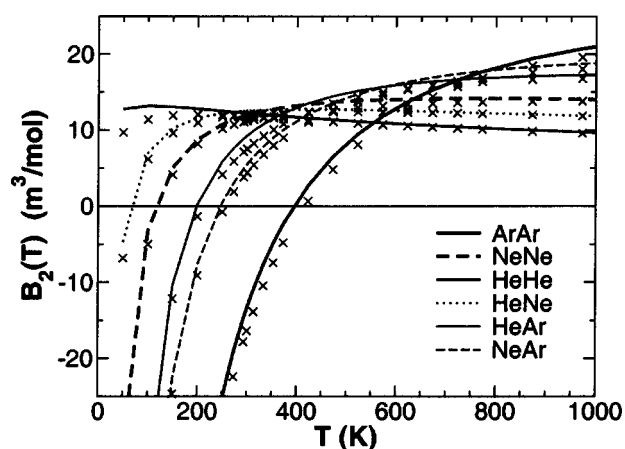


FIG. 3. Comparison of calculated second virial coefficients (lines) as a function of temperature with experimental values (\times marks) taken from Ref. 31.

metal mixtures. The agreement extends over a wide range of internuclear separations including regions of large “orbital overlap” on the repulsive wall (data not shown).

It should not be assumed that the excellent transferability among rare gases studied here will necessarily extend with the same reliability to molecules with dispersion interactions that are orientationally dependent, have vastly different average excitation energies or large hyperpolarizabilities. Nonetheless, this work provides useful benchmark data for the adaptation of simple models for the correlation energy that may be applied in bimolecular simulations, large-scale semiempirical quantum calculations, and hybrid quantum mechanical/molecular mechanical potentials where dispersion interactions are treated together with short-ranged “exchange” effects that are nonadditive⁴⁸ and corrupt transferability. Consequently, the development of new-generation force fields might benefit from treating the correlation energy separately from the short-ranged exchange interactions that might be modeled in a fundamentally different way: through a many-body framework that explicitly couples exchange with polarization terms such as has been suggested previously.⁴⁹

IV. CONCLUSION

High-level *ab initio* potential binding curves for rare gases have been presented over a large range of radial distances, and properties derivable from the two-body potentials have been examined. Overall, excellent agreement between experiment and theory are observed for the stationary points on the potential energy surface, and reasonable agreement is obtained for the second virial coefficients and Boyle temperatures. Analytic forms of the total binding energy, Hartree–Fock exchange, and correlation energies based on the calculated data are provided. It has been demonstrated that the contribution of the correlation energy for the heteronuclear dimers can be accurately modeled from the correlation energy of the homonuclear dimers using a simple geometric mean combining rule. These results serve as an important set of benchmark calculations and suggest new avenues for improvement of other empirical molecular mechanical and quantum models.

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