Open access • Journal Article • DOI:10.1080/00268970701843147

Ab initio pair potential energy curve for the argon atom pair and thermophysical properties of the dilute argon gas. I. Argon–argon interatomic potential and rovibrational spectra — Source link

Benjamin Jäger, Robert Hellmann, Eckard Bich, Eckhard Vogel

Institutions: University of Rostock

Published on: 13 Aug 2008 - Molecular Physics (Taylor & Francis Group)

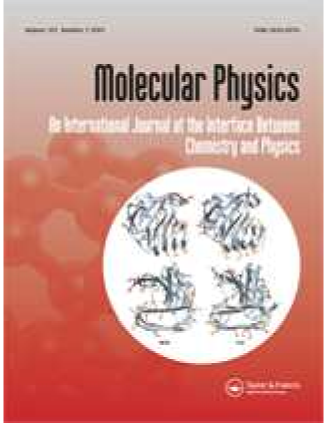
Topics: Interatomic potential, Ab initio, Lennard-Jones potential, Buckingham potential and Pair potential

Ab initio potential energy curve for the neon atom pair and thermophysical properties of the dilute neon gas. I. Neon-neon interatomic potential and rovibrational spectra

Eckhard Vogel, Robert Hellmann, Eckard Bich

▶ To cite this version:

Eckhard Vogel, Robert Hellmann, Eckard Bich. Ab initio potential energy curve for the neon atom pair and thermophysical properties of the dilute neon gas. I. Neon-neon interatomic potential and rovibrational spectra. Molecular Physics, Taylor & Francis, 2008, 106 (01), pp.133-140. 10.1080/00268970701843147 . hal-00513171



Ab initio potential energy curve for the neon atom pair and thermophysical properties of the dilute neon gas. I. Neon-neon interatomic potential and rovibrational spectra

Journal:	*Molecular Physics*
Manuscript ID:	TMPH-2007-0323.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	28-Nov-2007
Complete List of Authors:	Vogel, Eckhard; Universität Rostock, Institut für Chemie; Universität Rostock, Institut für Chemie Hellmann, Robert; Universität Rostock, Institut für Chemie Bich, Eckard; Universität Rostock, Institut für Chemie
Keywords:	Neon ab initio pair potential, neon analytical potential function, rovibrational spectra
Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.	
Neon1-MolPhys.tex	

Molecular Physics, Vol. 00, No. 00, DD Month 200x, 1–15

Ab initio potential energy curve for the neon atom pair and thermophysical properties of the dilute neon gas.

I. Neon-neon interatomic potential and rovibrational spectra

ROBERT HELLMANN, ECKARD BICH, and ECKHARD VOGEL*

Institut für Chemie, Universität Rostock, Albert-Einstein-Straße 3a, D-18059 Rostock,
Germany

(*Received 00 Month 200x; in final form 00 Month 200x*)

A neon-neon interatomic potential energy curve was derived from quantum-mechanical *ab initio* calculations using basis sets of up to t-aug-cc-pV6Z quality supplemented with bond functions and *ab initio* methods up to CCSDT(Q). In addition, corrections for relativistc effects were determined. An analytical potential function was fitted to the *ab initio* values and utilized to calculate the rovibrational spectra. The quality of the interatomic potential function was tested by comparison of the calculated spectra with experimental ones and those derived from other potentials of the literature. In a following paper the new interatomic potential is applied in the framework of the quantum-statistical mechanics and of the corresponding kinetic theory to determine selected thermophysical properties of neon governed by two-body and three-body interactions.

Keywords: Neon ab initio pair potential; neon analytical potential function; rovibrational spectra.

1 Introduction

In two recent papers [1,2] we demonstrated that the pair potential between two helium atoms can be determined very accurately using standard quantum chemistry software packages and that the thermophysical two-body and three-body properties of helium gas can be calculated with uncertainties which are superior to those of experimental data. Hence, the calculated properties can be applied as standard values over the complete range of temperatures from 1 K to 10,000 K.

The determination of the pair potential between two neon atoms is computationally much more demanding because of the increased number of electrons. But it could be expected that the thermophysical properties (especially transport properties) of neon, derived from a state-of-the-art pair potential, could serve as a second standard in combination with helium values for calibrating high-precision measur-

---

*Corresponding author. Email: eckhard.vogel@uni-rostock.de

Molecular Physics
ISSN 00268976 print/ISSN 13623028 online © 200x Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/0026897YYxxxxxxxx

ing instruments at low density and as starting points within the development of transport property surface correlations.

In this work it is intended to develop an accurate *ab initio* Ne-Ne interatomic potential based on CCSD(T) calculations using larger basis sets than previously possible and including an extrapolation to the complete basis set (CBS) limit. In addition, highly accurate corrections for neglected contributions should be included. In particular, the full T_3 operator should be taken into account by adding the differences in the interaction energies between CCSDT and CCSD(T), each determined with a smaller basis set, to the extrapolated CCSD(T) results. In an analogous manner corrections for perturbative quadruple excitations, core-core and core-valence correlations as well as scalar relativistic effects should be taken into account. Corrections for the breakdown of the Born-Oppenheimer approximation which had to be considered for the helium interaction potential are negligible for neon, because the neon isotopes are about five times heavier than ^{4}He. To the best of our knowledge, corrections arising from the Casimir-Polder retardation [3] have not yet been calculated for neon. The retardation effect is probably very small, but should be considered in future improvements of the potential.

The second priority objective of the present paper was to calculate rovibrational energy levels which should be used to compare with experimental data as a stringent test of the interatomic pair potential. Electronic absorption spectra of the neon dimer Ne_2 were investigated by Tanaka and Yoshino [4] in the vacuum ultraviolet (VUV) region with respect to the rotational structure and used to derive the potential well depth as well as the first two vibrational states and their rotational constants for the ground electronic state. Some other groups utilized the data of Tanaka and Yoshino together with high-energy beam scattering data and reliable values for different thermophysical properties of neon to determine semi-empirical potential curves for its ground electronic state from which the most recent one by Aziz and Slaman [5] is certainly the best. In 2003 Wüest and Merkt [6] performed new measurements of the transition between the $X0_g^+$ ground electronic state of Ne_2 and the second electronically excited state $\text{II}0_u^+$ using high-resolution VUV laser spectroscopy. They derived a map of the rovibrational energy level structure of the ground electronic state of the ^{20}Ne–^{20}Ne and of the ^{20}Ne–^{22}Ne dimers and determined a semi-empirical interaction potential for the neon dimer in its ground electronic state. The rovibrational energy levels calculated in this paper are to be compared particularly with the experimental ones by Wüest and Merkt.

2 Towards an accurate neon-neon interaction potential energy curve

The precise determination of the interatomic potentials between two rare gas atoms is not an easy task, whereas the demands grow with the increasing number of electrons of the respective atoms. The progress in the process of development towards an accurate neon-neon potential curve since 1999 is reported here in order to rank our work described in this paper.

In 1999 van Mourik et al. [7] derived an *ab initio* neon-neon potential comparably close to the semi-empirical potential curve of Aziz and Slaman [5]. The attractive part of the interaction potential is determined solely by dispersion due to electron correlation. To describe electron correlation accurately, large basis sets with many diffuse basis functions are needed. Hence van Mourik et al. [7] used for their calculations multi-augmented correlation-consistent basis sets of Dunning and coworkers up to t-aug-cc-pV5Z [8–10] and additionally a d-aug-cc-pV6Z basis set established by themselves. Suitable *ab initio* methods for determining the electron correlation within the supermolecular approach are many-body perturbation theory and coupled-cluster (CC) theory, the latter showing very fast convergence to the full configuration interaction (Full CI) limit. In particular, CCSD(T) (coupled-cluster theory with iterative singles and doubles excitations and noniterative perturbational treatment of triple excitations) [11] proved to be very successful in the calculations by van Mourik et al. [7] when using the counterpoise correction (CP) of Boys and Bernardi [12] for the basis set superposition error (BSSE) and extrapolating to the complete basis set (CBS) limit. Van Mourik et al. performed calculations in the range from $R = 0.267\,\mathrm{nm}$ to $R = 0.466\,\mathrm{nm}$, but reported only values for the well depth, for example, $40.92\,\mathrm{K}$ at $R = 0.310\,\mathrm{nm}$ for the CBS limit with d-aug-cc-pVXZ basis sets to be compared with $42.25\,\mathrm{K}$ at $R = 0.3091\,\mathrm{nm}$ for the potential by Aziz and Slaman [5]. In addition, van Mourik et al. investigated the core-core and core-valence correlation effects at the equilibrium distance and found them to be comparably small.

Van de Bovenkamp and van Duijneveldt [13] performed, also in 1999, CCSD(T) calculations with an interaction optimized basis set (IO240) including mid-bond functions (3s3p2d1f1g). They calculated the Ne-Ne interaction potential at internuclear separations between $R = 0.212\,\mathrm{nm}$ and $R = 0.476\,\mathrm{nm}$ and obtained a well depth of $40.99\,\mathrm{K}$ at $R = 0.310\,\mathrm{nm}$. Van de Bovenkamp and van Duijneveldt estimated that the missing attraction in their own potential compared with Aziz and Slaman should be due to basis set incompleteness, to incomplete consideration of triple and higher excitations, and to relativistic effects. Cybulski and Toczylowski [14] used CCSD(T) together with the aug-cc-pV5Z basis set and a set of mid-bond functions (3s3p2d2f1g) for their calculations of the potential energy curve in the range between $R = 0.225\,\mathrm{nm}$ and $R = 0.500\,\mathrm{nm}$ and determined a well depth of $41.19\,\mathrm{K}$ at $R = 0.30988\,\mathrm{nm}$ (the fitted potential has a well depth of $41.15\,\mathrm{K}$) which is also smaller than that of the semi-empirical potential of Aziz and Slaman [5]. Van de Bovenkamp and van Duijneveldt as well as Cybulski and Toczylowski used the counterpoise procedure for the BSSE, but did not perform any extrapolation to the CBS limit and did not consider core-core and core-valence contributions. However, they proved the importance of the use of bond functions. Here caution is needed if bond functions are used with small atom-centred basis sets, since they can lead to serious imbalance effects as was shown for the Ne-Ne potential by Grochola et al. [15]. Fortunately, computational advances allow to use comparably large basis sets today for Ne-Ne so that imbalance effects can be avoided.

Gdanitz [16] applied the results of Cybulski and Toczylowski and added basic corrections for basis set incompleteness, for Full CI, for core-core and core-valence correlation as well as for scalar relativistic effects resulting in a well depth of 41.535 K at $R = 0.31007$ nm. No analytical potential function was given in this paper. A potential fit was done later by Venkatraj et al. [17] and used in molecular dynamics simulations of gaseous and liquid neon [17] and in Monte Carlo simulations of the vapor-liquid equilibria [18]. Giese et al. [19] extended the calculations of Cybulski and Toczylowski to a larger number of internuclear separations (100 distances) and performed separate fits for the repulsive (SCF) part of the potential and for the attractive (correlation) part, whereas the fit of Cybulski and Toczylowski for the whole potential was left unchanged. Nasrabad et al. [20] extrapolated the results of Cybulski and Toczylowski to the complete basis set limit. The resulting potential has a well depth of 41.35 K at $R = 0.3097$ nm. It was used together with a non-additive three-body contribution for Monte Carlo simulations of the vapor-liquid equilibria. Lee [21] carried out CCSDT [22] calculations at $R = 0.31$ nm and added the difference between CCSDT und CCSD(T) to the CCSD(T) result of 41.19 K from Cybulski and Toczylowski to estimate the binding energy of the dimer. He found a well depth of 41.87 K which shows that missing triple contributions in CCSD(T) are the main reason for the disagreement between CCSD(T) potentials and the potential of Aziz and Slaman.

3 Quantum chemical determination and analytical representation of the Ne-Ne potential

The interaction energies were determined for 32 different Ne-Ne distances between $R = 0.14$ nm and $R = 0.80$ nm which is sufficient for the fit of an analytical potential function. All calculations were performed using the supermolecular approach including a full counterpoise correction [12] as follows:

$$V(R) = \Delta E_{\mathrm{Ne-Ne}}(R) = E_{\mathrm{Ne-Ne}}(R) - 2\ E_{\mathrm{Ne-Q}}(R)\ . \qquad (1)$$

Here $E_{\mathrm{Ne-Q}}(R)$ corresponds to the energy of a neon atom with a ghost basis set at the distance R.

First, CCSD(T) calculations were performed within the frozen-core approximation using the t-aug-cc-pV5Z and t-aug-cc-pV6Z basis sets, each supplemented by a (4s4p3d3f2g) set of bond functions centred between the two atoms. The bond function exponents are: *sp*: 0.06, 0.18, 0.54, 1.62; *df*: 0.15, 0.45, 1.35; *g*: 0.3, 0.9. These basis sets (and in an analogous manner all further basis sets) are abbreviated as taV5Z+(44332) and taV6Z+(44332). For each separation R the correlation part of the CCSD(T) interaction energies $V_{\mathrm{CCSD(T)corr}}$ obtained with these two basis sets was extrapolated to the CBS limit with the formula proposed by Halkier et al. [23]:

$$V^{\mathrm{taV}X\mathrm{Z}}_{\mathrm{CCSD(T)\,corr}} = V^{\mathrm{CBS}}_{\mathrm{CCSD(T)\,corr}} + \alpha X^{-3} \,. \tag{2}$$

The SCF interaction energies were not extrapolated and taken from the taV6Z+(44332) calculations.

Corrections for missing core-core and core-valence correlation, relativistic effects as well as for higher coupled-cluster contributions were added to the CCSD(T) interaction energies:

$$V = V^{\mathrm{CBS}}_{\mathrm{CCSD(T)}} + \Delta V_{\mathrm{core}} + \Delta V_{\mathrm{rel}} + \Delta V_{\mathrm{T-(T)}} + \Delta V_{\mathrm{(Q)}} \,. \tag{3}$$

The correction for core-core and core-valence correlation ΔV_{core} was estimated using the dawCV5Z basis set [24] by computing the differences between the interaction energies at the all-electron CCSD(T) level and at the frozen-core CCSD(T) level. The effect is relatively small at the equilibrium distance (+0.068 K at $R = 0.31$ nm), but becomes rather large at small distances (-110.5 K at $R = 0.14$ nm).

The correction for scalar relativistic effects ΔV_{rel} was also computed at the all-electron CCSD(T)/dawCV5Z level within the so-called Cowan-Griffin approximation [25]. The resulting correction is negative for all distances and similar in magnitude to ΔV_{core}.

Missing triple contributions in the CCSD(T) calculations were estimated using a daVQZ+(3321) basis set (exponents of the bond functions: *sp*: 0.1, 0.3, 0.9; *d*: 0.25, 0.75; *f*: 0.45) in the non-relativistic frozen-core approximation by calculating the differences between the interaction energies at the CCSDT and CCSD(T) levels of theory. The resulting correction $\Delta V_{\mathrm{T-(T)}}$ is much larger than ΔV_{core} and ΔV_{rel} at equilibrium distance (-0.646 K at $R = 0.31$ nm) and relatively unimportant at small distances (-8.57 K at $R = 0.14$ nm).

The correction $\Delta V_{\mathrm{(Q)}}$ resulting from the noniterative perturbational treatment of connected quadruple excitations was determined in a similar way as $\Delta V_{\mathrm{T-(T)}}$. The differences between the CCSDT(Q) [26] and CCSDT interaction energies were calculated with an aVTZ+(3321) basis set (exponents of the bond functions equal to the ones used for the triples contribution correction). At large R, numerical inaccuracies turned out to be problematic. Hence the results for distances between

$R = 0.38\,\mathrm{nm}$ and $R = 0.50\,\mathrm{nm}$ had to be smoothed with a polynomial, whereas the results for distances larger than $R = 0.50\,\mathrm{nm}$ were extrapolated by assuming that the ratio between this correction and the total correlation interaction energy is constant. The correction $\Delta V_{(\mathrm{Q})}$ is very small and amounts to only -0.091 K at $R = 0.31\,\mathrm{nm}$ which shows that CCSDT(Q) is very close to the Full CI limit and that CCSDT is a good approximation to Full CI for the calculation of interaction energies.

All *ab initio* results are given in Tables 1 and 2. The CCSD(T) calculations were performed with PSI3 [27] and with the Mainz-Austin-Budapest version of ACES II [28] which was also used for the CCSDT computations and for the determination of the relativistic corrections. The CCSDT(Q) calculations were carried out using the general coupled-cluster code MRCC of Kállay [29].

A modification of the potential function given by Tang and Toennies [30] was fitted to the *ab initio* interaction energies:

$$\begin{aligned} V(R) = {} & A \exp(a_1 R + a_2 R^2 + a_{-1} R^{-1} + a_{-2} R^{-2}) \\ & - \sum_{n=3}^{8} \frac{C_{2n}}{R^{2n}} \left[1 - \exp(-bR) \sum_{k=0}^{2n} \frac{(bR)^k}{k!} \right] , \end{aligned} \tag{4}$$

The coefficients A, a_1, a_2, a_{-1}, a_{-2}, b as well as the dispersion coefficients C_6, C_8, and C_{10} were fitted independently. The higher dispersion coefficients were simultaneously determined within the fit using the recursion formula [30]:

$$C_{2n} = C_{2n-6} \left(\frac{C_{2n-2}}{C_{2n-4}} \right)^3 , \qquad n \geq 6 \; . \tag{5}$$

Deviations between calculated and fitted potential energies are smaller than ±0.1 % for all distances except for $R = 0.80\,\mathrm{nm}$, where the difference is slightly larger. The fitted dispersion coefficients C_6, C_8, and C_{10} are in very good agreement with the *ab initio* dispersion coefficients derived by Thakkar et al. [31] using many-body perturbation theory. The resulting potential function has a well depth of 42.153 K at a distance of $R = 0.30895\,\mathrm{nm}$. This comes very close to the corresponding values of the potential of Aziz and Slaman [5] with a well depth of 42.25 K at a distance of $R = 0.3091\,\mathrm{nm}$. The potential parameters are listed in Table 3.

4 Vibrational and rotational energy levels

A very direct and stringent test of any potential energy curve consists in the calculation of the energy differences for the rovibrational transitions in the ground electronic state. For that purpose the program LEVEL 7.7 by Le Roy [32] was used. The results for the ^{20}Ne–^{20}Ne and the ^{20}Ne–^{22}Ne dimers calculated for the potential energy curves of Aziz and Slaman [5], of Cybulski and Toczylowski [14], of Wüest and Merkt [6] as well as of the present paper are listed in Table 4 and Table 5. In general, three vibrational states were found for both dimers, whereas the energy of each ground vibrational state $v = 0$ is only at about 60% of the dissociation energy ($-D_e = -42.153\,\mathrm{K}$) characterizing the weakly bound nature of the potential. The energies for the rotationally excited states differ from that of the $J = 0$ states by the addition of the centrifugal potential. Only the bound states with negative energies E_{vJ} are accessible with the experimental arrangement by Wüest and Merkt [6], whereas the lifetimes for the quasibound levels with positive energies are too short.

As shown in Table 4, Wüest and Merkt [6] observed actually nine of the ten bound rovibrational levels of the ^{20}Ne–^{20}Ne dimer. The energy differences calculated for the potential of Wüest and Merkt agree of course with the observed values of these authors within the uncertainties of the spectra (numbers in brackets in the third column of the table), since the potential energy curve was derived on the basis of these observed data. The deviations between the energy differences calculated with the new potential of this paper and the observed values for $v = 0$ increase with increasing J and exceed the experimental uncertainties for higher J. On the contrary, the deviations between the values for the new potential and the observed data for $v = 1$ are in reasonable agreement because of the ten times higher experimental uncertainties. The same findings result from a comparison of the values calculated for the semi-empirical potential by Aziz and Slaman [5] and of the observed data by Wüest and Merkt [6]. In addition, the values calculated for the potentials of Aziz and Slaman and of the present paper agree with each other better than with the observed data for $v = 0$. Finally, the values determined from the potential by Cybulski and Toczylowski [14] show comparably large deviations from the experimentally observed data.

Table 5 illustrates that the spectra of the ^{20}Ne–^{22}Ne dimer are of poorer quality and characterized by larger experimental uncertainties. Hence, only five of altogether 18 bound rovibrational levels were found by Wüest and Merkt [6]. Furthermore, the values calculated for all four considered potentials agree within the experimental uncertainties with the observed data.

In Table 6 the dissociation energy D_e, the equilibrium internuclear distance R_ε, the vibrational-ground-state dissociation energy D_{00}, and the vibrational interval $\Delta G_{1/2}$ of the ^{20}Ne–^{20}Ne dimer in the ground electronic state are compared for the considered potential energy curves including that of Gdanitz [16]. The table makes evident that the semi-empirical potential by Aziz and Slaman fitted primarily to different experimental data, the potential by Wüest and Merkt [6] adjusted to their rovibrational spectra, and the potential of this paper derived from quantum-mechanical *ab initio* calculations are in close agreement.

5 Summary and conclusions

The interaction energies for the neon atom pair were calculated for a large number of interatomic separations. Basis sets of up to t-aug-cc-pV6Z quality with bond functions at the CCSD(T) level were utilized. In addition, highly accurate corrections for higher-order coupled-cluster excitations up to CCSDT(Q) as well as corrections for core-core and core-valence correlations and for scalar relativistic effects were determined. It could be shown that, when going from CCSD(T) to CCSDT, the well depth increases considerably, whereas a further enhancement to CCSDT(Q) has only a marginal effect.

An analytical potential function was fitted to the ab initio values and used to derive the rovibrational spectra of the ^{20}Ne–^{20}Ne and ^{20}Ne–^{22}Ne dimers in the ground electronic state. These values were compared with highly accurate experimental data of Wüest and Merkt [6] and with values calculated for other potential energy curves from the literature. The comparison makes evident that the potentials of Aziz and Slaman [5], of Wüest and Merkt [6], and of the present paper are in close agreement. One should keep in mind that the rovibrational spectra are essentially governed by the attractive part of the potential around its minimum. Hence a comprehensive comparison with experimental data for the transport properties, which are strongly influenced by the repulsive part of the potential, represents a further stringent test and will become the focus of the second paper of this series [33].

References

[1] R. Hellmann, E. Bich, and E. Vogel, *Mol. Phys.*, submitted.

[2] E. Bich, R. Hellmann, and E. Vogel, *Mol. Phys.*, submitted.

[3] H. B. G. Casimir and D. Polder, *Phys. Rev.*, **73**, 360 (1948).

[4] Y. Tanaka and K. Yoshino, *J. Chem. Phys.*, 57, 2964 (1972).

[5] R. A. Aziz and M. J. Slaman, *Chem. Phys.*, **130**, 187 (1989).

[6] A. Wüest and F. Merkt, *J. Chem. Phys.*, 118, 8807 (2003).

[7] T. van Mourik, A. K. Wilson, and T. H. Dunning, Jr., *Mol. Phys.*, **96**, 529 (1999).

[8] T. H. Dunning, Jr., *J. Chem. Phys.*, **90**, 1007 (1989).

[9] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.*, **96**, 6796 (1992).

[10] D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.*, **100**, 2975 (1994).

[11] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.*, **157**, 479 (1989).

[12] S. F. Boys and F. Bernardi, *Mol. Phys.*, **19**, 553 (1970).

[13] J. van de Bovenkamp and F. B. van Duijneveldt, *Chem. Phys. Lett.*, **309**, 287 (1999).

[14] S. M. Cybulski and R. R. Toczylowski, *J. Chem. Phys.*, **111**, 10520 (1999).

[15] G. Grochola, T. Petersen, S. P. Russo, and I. K. Snook, *Mol. Phys.*, **100**, 3867 (2002).

[16] R. J. Gdanitz, *Chem. Phys. Lett.*, **348**, 67 (2001).

[17] M. Venkatraj, M. G. Müller, H. Huber and R. J. Gdanitz, *Collect. Czech. Chem. Commun.*, **68**, 627 (2003).

[18] M. Venkatraj, C. Bratschi, H. Huber, and R. J. Gdanitz, *Fluid Phase Eq.*, **218**, 285 (2004).

[19] T. J. Giese, V. M. Audette, and D. M. York, *J. Chem. Phys.*, **119**, 2618 (2003).

[20] A. E. Nasrabad, R. Laghaei, and U. K. Deiters, *J. Chem. Phys.*, **121**, 6423 (2004).

[21] J. S. Lee, *Theor. Chem. Acc.*, **113**, 87 (2005).

[22] J. Noga and R. J. Bartlett, *J. Chem. Phys.*, **86**, 7041 (1987), Erratum *J. Chem. Phys.*, **89**, 3401 (1988).

[23] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.*, **286**, 243 (1998).

[24] K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.*, **117**, 10548 (2002).

[25] R. D. Cowan and D. C. Griffin, *J. Opt. Soc. Am.*, **66**, 1010 (1976).

[26] M. Kállay and J. Gauss, *J. Chem. Phys.*, **123**, 214105 (2005).

[27] "PSI3: An Open-Source Ab Initio Electronic Structure Package", T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, R. A. King, M. L. Leininger, S. T. Brown, C. L. Janssen, E. T. Seidl, J. P. Kenny, and W. D. Allen, *J. Comp. Chem.*, **28**, 1610 (2007).

[28] J. F. Stanton, J. Gauss, J. D. Watts, P. G. Szalay, and R. J. Bartlett, with contributions from A. A. Auer, D. B. Bernholdt, O. Christiansen, M. E. Harding, M. Heckert, O. Heun, C. Huber, D. Jonsson, J. Jusélius, W. J. Lauderdale, T. Metzroth, C. Michauk, D. R. Price, K. Ruud, F. Schiffmann, A. Tajti, M. E. Varner, J. Vázquez, and the integral packages: MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), and ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen). See, also J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, *Int. J. Quantum Chem. Symp.*, **26**, 879 (1992). Current version see http://www.aces2.de.

[29] MRCC, a string-based general coupled cluster program suite written by M. Kállay. See also M. Kállay and P. R. Surján, *J. Chem. Phys.*, **115**, 2945 (2001) as well as: http://www.mrcc.hu.

[30] K. T. Tang and J. P. Toennies, *J. Chem. Phys.*, **80**, 3726 (1984).

[31] A. J. Thakkar, H. Hettema, and P. E. S. Wormer, *J. Chem. Phys.*, 97, 3252 (1992).

[32] R. J. Le Roy, *Level 7.7: A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels*, University of Waterloo, Chemical Physics Research Report No. CP-661, Waterloo, Ontario, Canada.

[33] E. Bich, R. Hellmann, and E. Vogel, in preparation.

Table 1. Ne-Ne SCF and CCSD(T) interaction energies for the taV5Z+(44332) and taV6Z+(44332) basis sets and the extrapolated CCSD(T) values. All energies are in Kelvin.

R/nm	V(SCF)		V(CCSD(T))		
	taV5Z+(44332)	taV6Z+(44332)	taV5Z+(44332)	taV6Z+(44332)	extrapolated
0.14	71550.433	71548.487	69122.802	69044.386	68939.345
0.16	28504.771	28503.861	27107.732	27067.581	27013.678
0.18	11385.933	11385.622	10504.957	10486.497	10461.566
0.20	4551.060	4550.932	3966.717	3957.967	3946.125
0.22	1817.497	1817.446	1421.412	1417.452	1412.082
0.24	724.521	724.515	454.750	453.070	450.770
0.25	457.077	457.078	234.567	233.499	232.029
0.26	288.193	288.196	104.787	104.124	103.208
0.27	181.605	181.610	30.507	30.110	29.559
0.28	114.373	114.379	-10.086	-10.314	-10.634
0.29	71.991	71.997	-30.554	-30.678	-30.855
0.30	45.290	45.295	-39.279	-39.328	-39.401
0.31	28.478	28.481	-41.357	-41.362	-41.375
0.32	17.897	17.900	-39.870	-39.855	-39.840
0.33	11.241	11.245	-36.658	-36.626	-36.587
0.34	7.057	7.060	-32.765	-32.726	-32.678
0.35	4.428	4.431	-28.773	-28.737	-28.690
0.36	2.778	2.780	-25.000	-24.962	-24.913
0.37	1.741	1.743	-21.576	-21.542	-21.497
0.38	1.092	1.093	-18.555	-18.523	-18.481
0.40	0.428	0.429	-13.673	-13.651	-13.623
0.42	0.167	0.168	-10.114	-10.094	-10.068
0.44	0.065	0.066	-7.542	-7.526	-7.505
0.46	0.026	0.026	-5.684	-5.671	-5.654
0.48	0.010	0.010	-4.329	-4.323	-4.314
0.50	0.004	0.004	-3.338	-3.333	-3.325
0.52	0.002	0.002	-2.603	-2.597	-2.589
0.56	0.000	0.000	-1.629	-1.626	-1.621
0.60	0.000	0.000	-1.056	-1.055	-1.052
0.65	0.000	0.000	-0.641	-0.640	-0.639
0.70	0.000	0.000	-0.405	-0.405	-0.404
0.80	0.000	0.000	-0.178	-0.178	-0.178

Table 2. Corrections to the extrapolated CCSD(T) interaction energies and the final potential values. All energies are in Kelvin.

R/nm	ΔV_{core} dawCV5Z	ΔV_{rel} dawCV5Z	$\Delta V_{\mathrm{T-(T)}}$ daVQZ+(3321)	$\Delta V_{\mathrm{(Q)}}$ aVTZ+(3321)	$V(R)$
0.14	-110.504	-197.556	-8.572	11.597	68634.310
0.16	-52.833	-77.901	-7.131	4.128	26879.940
0.18	-24.471	-29.825	-5.560	0.453	10402.164
0.20	-10.933	-11.126	-4.124	-0.964	3918.978
0.22	-4.647	-4.074	-2.975	-1.159	1399.226
0.24	-1.827	-1.487	-2.124	-0.888	444.443
0.25	-1.093	-0.906	-1.793	-0.747	227.490
0.26	-0.620	-0.561	-1.513	-0.558	99.956
0.27	-0.321	-0.356	-1.277	-0.420	27.186
0.28	-0.136	-0.234	-1.077	-0.307	-12.388
0.29	-0.026	-0.161	-0.908	-0.215	-32.165
0.30	0.036	-0.116	-0.766	-0.145	-40.392
0.31	0.068	-0.087	-0.646	-0.091	-42.130
0.32	0.082	-0.069	-0.544	-0.052	-40.423
0.33	0.086	-0.056	-0.459	-0.024	-37.040
0.34	0.082	-0.046	-0.387	-0.002	-33.032
0.35	0.076	-0.039	-0.327	0.008	-28.972
0.36	0.069	-0.033	-0.277	0.017	-25.137
0.37	0.061	-0.029	-0.234	0.021	-21.678
0.38	0.053	-0.025	-0.199	0.022	-18.629
0.40	0.040	-0.019	-0.144	0.023	-13.723
0.42	0.030	-0.014	-0.105	0.020	-10.136
0.44	0.023	-0.011	-0.078	0.017	-7.554
0.46	0.017	-0.008	-0.058	0.014	-5.690
0.48	0.013	-0.006	-0.044	0.011	-4.340
0.50	0.010	-0.005	-0.034	0.009	-3.345
0.52	0.008	-0.004	-0.026	0.007	-2.605
0.56	0.005	-0.002	-0.016	0.004	-1.631
0.60	0.003	-0.002	-0.010	0.003	-1.058
0.65	0.002	-0.001	-0.006	0.002	-0.643
0.70	0.001	-0.001	-0.004	0.001	-0.406
0.80	0.001	0.000	-0.002	0.000	-0.179

Table 3. Potential parameters

Parameter	Unit	Value	Thakkar et al. [31]
A	K	$4.02915058383 \times 10^{7}$	
a_1	$(\mathrm{nm})^{-1}$	$-4.28654039586 \times 10^{1}$	
a_2	$(\mathrm{nm})^{-2}$	-3.33818674327	
a_{-1}	nm	$-5.34644860719 \times 10^{-2}$	
a_{-2}	$(\mathrm{nm})^{2}$	$5.01774999419 \times 10^{-3}$	
b	$(\mathrm{nm})^{-1}$	$4.92438731676 \times 10^{1}$	
C_6	$\mathrm{K}\,(\mathrm{nm})^{6}$	$4.40676750157 \times 10^{-2}$	4.54364×10^{-2}
C_8	$\mathrm{K}\,(\mathrm{nm})^{8}$	$1.64892507701 \times 10^{-3}$	1.75423×10^{-3}
C_{10}	$\mathrm{K}\,(\mathrm{nm})^{10}$	$7.90473640524 \times 10^{-5}$	8.34962×10^{-5}
C_{12}	$\mathrm{K}\,(\mathrm{nm})^{12}$	$4.85489170103 \times 10^{-6}$	
C_{14}	$\mathrm{K}\,(\mathrm{nm})^{14}$	$3.82012334054 \times 10^{-7}$	
C_{16}	$\mathrm{K}\,(\mathrm{nm})^{16}$	$3.85106552963 \times 10^{-8}$	
$\varepsilon/k_{\mathrm{B}}$	K	42.152521	
R_{ε}	nm	0.30894556	
σ	nm	0.27612487	

Table 4. Energy differences between the rotational levels for the three vibrational states of the electronic ground state of the $^{20}\mathrm{Ne}-{}^{20}\mathrm{Ne}$ dimer and comparison between values calculated for different potential energy curves and the observed values by Wüest und Merkt [6]. Last column: energy calculated for the potential of the present paper to be compared with the dissociation energy: $-D_\mathrm{e} = -42.153\,\mathrm{K}$.

		Observed	Calculated differences for the potential energy curves by				Calculated
		Wüest, Merkt [6]	Aziz, Slaman [5]	Cybulski, Toczylowski [14]	Wüest, Merkt [6]	present	energy present
v	J	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}}{\mathrm{K}}$
0	0	0.0	0.0	0.0	0.0	0.0	−24.0941
0	2	0.937(10)	0.9333	0.9266	0.9300	0.9338	−22.7506
0	4	3.088(10)	3.0984	3.0757	3.0875	3.1001	−19.6338
0	6	6.426(18)	6.4630	6.4145	6.4406	6.4666	−14.7901
0	8	10.947(19)	10.9691	10.8833	10.9319	10.9753	−8.3031
0	10	16.464(26)	16.5159	16.3769	16.4608	16.5247	−0.3187
0	12		22.8836	22.6512	22.8044	22.8877	8.8362
0	14		29.8065				
1	0	13.76(14)	13.8443	13.4551	13.7746	13.7928	−4.2494
1	2	14.36(14)	14.4514	14.0478	14.3756	14.3944	−3.3838
1	4	15.73(14)	15.8174	15.3762	15.7275	15.7455	−1.4398
1	6		17.7436	17.2201	17.6321	17.6352	1.2791
2	0		16.9199	16.2551	16.8146	16.7333	−0.0187

Table 5. Energy differences between the rotational levels for the three vibrational states of the electronic ground state of the ^{20}Ne–^{22}Ne dimer and comparison between values calculated for different potential energy curves and the observed values by Wüest und Merkt [6]. Last column: energy calculated for the potential of the present paper to be compared with the dissociation energy: $-D_e = -42.153\,\mathrm{K}$.

		Observed Wüest, Merkt [6]	Calculated differences for the potential energy curves by Aziz, Slaman [5]	Cybulski, Toczylowski [14]	Wüest, Merkt [6]	present	Calculated energy present
v	J	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}-E_{00}}{\mathrm{cm}^{-1}}$	$\frac{E_{vJ}}{\mathrm{K}}$
0	0	0.0	0.0000	0.0000	0.0000	0.0000	−24.4466
0	1		0.2983	0.2962	0.2973	0.2985	−24.0172
0	2	0.896(51)	0.8940	0.8876	0.8908	0.8945	−23.1597
0	3	1.791(76)	1.7851	1.7722	1.7788	1.7861	−21.8769
0	4	2.92(11)	2.9686	2.9471	2.9583	2.9703	−20.1731
0	5	4.35(19)	4.4404	4.4079	4.4251	4.4430	−18.0542
0	6		6.1949	6.1491	6.1738	6.1986	−15.5282
0	7		8.2251	8.1633	8.1974	8.2301	−12.6054
0	8		10.5217	10.4411	10.4867	10.5282	−9.2989
0	9		13.0728	12.9699	13.0297	13.0809	−5.6261
0	10		15.8622	15.7325	15.8103	15.8718	−1.6107
0	11		18.8662	18.7033	18.8046	18.8765	2.7125
0	12		22.0429	21.8327	21.9698	22.0511	7.2800
0	13		25.3217	25.0583	25.2351	25.3268	11.9929
0	14		28.7526	28.4745	28.6602	28.7706	16.9479
1	0		13.8240	13.4465	13.7604	13.7803	−4.6198
1	1		14.0228	13.6409	13.9573	13.9775	−4.3362
1	2		14.4170	14.0261	14.3476	14.3684	−3.7738
1	3		14.9996	14.5945	14.9243	14.9455	−2.9433
1	4		15.7581	15.3327	15.6751	15.6961	−1.8634
1	5		16.6715	16.2170	16.5787	16.5978	−0.5661
1	6		17.6953	17.1917	17.5908	17.6003	0.8762
1	7		18.7871		18.6701	18.6865	2.4390
2	0		17.1421	16.4813	17.0373	16.9606	−0.0441
2	1		17.1860	17.0825			

Table 6. Dissociation energy D_e, equilibrium internuclear distance R_ε, vibrational-ground-state dissociation energy D_{00}, and vibrational interval $\Delta G_{1/2}$ of the ^{20}Ne–^{20}Ne dimer in the ground electronic state for different potential energy curves.

D_e K	R_ε nm	D_{00} K	$\Delta G_{1/2}$ K	Reference
42.25	0.3091	24.07	19.91	Aziz, Slaman [5]
41.155	0.30988	23.399	19.37	Cybulski, Toczylowski [6]
41.535±0.29	0.31007±0.0002	23.605±0.29	19.592±0.14	Gdanitz [16]
42.30±0.17	0.3094±0.0001	24.22	19.82±0.17	Wüest, Merkt [6]
42.153	0.30895	24.094	19.845	present