Rydberg-London Potential for Diatomic Molecules and Unbonded Atom Pairs

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We propose and test a pair potential that is accurate at all relevant distances and simple enough for use in large-scale computer simulations. A combination of the Rydberg potential from spectroscopy and the London inverse-sixth-power energy, the proposed form fits spectroscopically determined potentials better than the Morse, Varnshi, and Hulburt-Hirschfelder potentials and much better than the Lennard-Jones and harmonic potentials. At long distances, it goes smoothly to the correct London force appropriate for gases and preserves van der Waals’s “continuity of the gas and liquid states,” which is routinely violated by coefficients assigned to the Lennard-Jones 6-12 form.

There are at least three classes of interatomic potentials. Commercial codes use the Lennard-Jones
\begin{equation}
V_{LJ}(r) = |V(r_0)| \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \tag{1}
\end{equation}
and harmonic
\begin{equation}
V_H(r) = V(r_0) + \frac{(r - r_0)^2}{2} \frac{d^2V(r_0)}{dr^2} \tag{2}
\end{equation}
forms, which are accurate near the minimum at \( r = r_0 \). But this first class of potentials may be too simple for complex materials away from equilibrium.

The Morse
\begin{equation}
V_M(r) = |V(r_0)| \left( 1 - e^{-\kappa x} \right)^2 - 1 \tag{3}
\end{equation}
\((x = r - r_0, \kappa = \sqrt{k_e/(2|V(r_0)|)}), \text{ Varnshi} \tag{2} \)
\begin{equation}
V_V(r) = |V(r_0)| \left( 1 - \frac{r_0}{r} e^{-\beta (r^2 - r_0^2)} \right)^2 - 1, \tag{4}
\end{equation}
\((\beta = (\kappa r_0^2 - 1)/(2r_0^2)), \text{ and Hulburt-Hirschfelder} \tag{3} \)
\begin{equation}
V_{HH}(r) = V_M(r) + |V(r_0)| c' \kappa x^3 e^{-2\kappa x} (1 + \kappa b' x) \tag{5}
\end{equation}
\((\text{for } b', c', \text{ see ref.} 4) \) potentials represent a second class of potentials \( \text{a} \) accurate over a wider range of distances.

Quantum chemists \( \text{b, c, d, e} \) have derived a third class that reproduce spectroscopic and thermodynamic data with impressive fidelity. But the potentials of this class involve many parameters and may be too cumbersome for use in large-scale simulations.

We propose and test a form
\begin{equation}
V(r) = ae^{-br} (1 - cr) - \frac{d}{r^6 + e r^{-6}} \tag{6}
\end{equation}
that is nearly as accurate as the class-3 potentials but simpler than many class-2 potentials. It is a combination of the Rydberg formula used in spectroscopy and the London formula for pairs of atoms. In Eq. 4, the terms involving \( a, b, \) and \( c \) were proposed by Rydberg \( 10 \) to incorporate spectroscopic data, but were largely ignored until recently \( 11, 12 \). The constant \( d = C_6 \) is the coefficient of the London tail. The new term \( e r^{-6} \) cures the London singularity. As \( r \to 0 \), \( V(r) \to a \), finite; as \( r \to \infty \), \( V(r) \) approaches the London term, \( V(r) \to -d/r^6 = -C_6/r^6 \). In a perturbative analysis \( 13 \), the \( a, b, c \) terms arise in first order, and the \( d \) term in second order.

To test whether the hybrid \( V(r) \) can represent covalent bonds far from equilibrium, we used Gnuplot \( 14 \) to fit Eq. 4 to empirical potentials for molecular \( H_2, N_2, \) and
FIG. 2: The hybrid form \( V \) (Eq. (6) as in Fig. 1, solid, red) fits the RKR spectral points for the ground state of molecular hydrogen (pluses, blue). The Morse \( V_M \) (Eq. (3), dashes, green), Varnshi \( V \) (Eq. (4), dots, magenta), and Hulburt-Hirschfelder \( V_H \) (Eq. (5), dot-dash, cyan) are too low for \( 1.5 < r < 2 \) Å.

FIG. 3: For the ground state of molecular nitrogen, the proposed potential \( V \) of Eq. (6) (with \( a = 3.25 \) keV, \( b = 4.30 \) Å\(^{-1}\), \( c = 1.1906 \) Å\(^{-1}\), \( d = 14.1 \) eV Å, and \( e = 27.1 \) Å\(^2\)) (solid, red) fits the RKR spectral points (pluses, blue) and the FO points (x’s, cyan). \( V_{LJ} \) and \( V_H \) as in Fig. 1.

FIG. 4: For the ground state of molecular nitrogen, the hybrid form \( V \) (Eq. (6), as in Fig. 3, solid, red) fits the RKR spectral points (pluses, blue) and the FO points (x’s, black). \( V_M \), \( V_V \), & \( V_H \) as in Fig. 2.

FIG. 5: For the ground state of molecular oxygen, the potential \( V \) of Eq. (6) (with \( a = 3.61 \) keV, \( b = 4.48 \) Å\(^{-1}\), \( c = 1.05 \) Å\(^{-1}\), \( d = 16.08 \) eV Å\(^6\), and \( e = 58.4 \) Å\(^2\)) (solid, red) fits the RKR points (pluses, blue). \( V_{LJ} \) and \( V_H \) as in Figs. 1 & 3.

O\(_2\) obtained from spectroscopic data [15, 16, 17] by the RKR (Rydberg [10], Klein [18], Rees [19]) method, setting \( d \) equal to the London values. Figure 1 shows that the hybrid potential of Eq. (6) (solid, red) goes through the RKR points for H\(_2\) (pluses, blue) from 0.5 to 4 Å. Fitted to the minimum, the harmonic potential \( V_H \) (dashes, green) and the Lennard-Jones potential \( V_{LJ} \) (dashes, blue) are accurate only near the minimum at 0.74 Å. Figures 3 & 5 show that the hybrid potential \( V(r) \) fits the N\(_2\) and O\(_2\) RKR points [10, 17] and the N\(_2\) first-order (FO) points [20] between 1 and 1.8 Å. The Lennard-Jones and harmonic potentials of Eqs. 1 & 2 fit only near the minima.

How does the hybrid form compare with the class-2 potentials of Eqs. 3–5? Figures 2, 4 & 6 show that for \( 1.4 < r < 2 \) Å the hybrid \( V(r) \) is closer than 35.
FIG. 6: For the ground state of molecular oxygen, the hybrid form $V$ (Eq. (6), as in Fig. 5, solid, red) fits the RKR spectral points (pluses, blue). $V_M$, $V_V$, and $V_{HH}$ as in Fig. 2.

FIG. 7: The potential $V$ (Eq. (6) for the Ar-Ar ground state with $a = 1720$ eV, $b = 2.6920$ Å$^{-1}$, $c = 0.2631$ Å$^{-1}$, $d = 37.943$ eV Å$^6$, and $e = 177588$ Å$^{12}$) (solid, red) fits the Ar$_2$ Aziz potential (pluses, blue) with the correct London tail. When matched at the minimum, the Lennard-Jones form $V_{LJ}$ (Eq. (1) with $r_0 = 3.757$ Å and $V(r_0) = -0.01234$ eV) (dashes, green) is too low for $r > 4$ Å.

To the RKR points. A useful estimate of how well a particular potential $V_P(r)$ fits $N$ data points $V_D(r_i)$ is the dimensionless error

$$\delta = \frac{1}{|V_D(r_0)|} \left[ \frac{1}{N} \sum_{i=1}^{N} (V_P(r_i) - V_D(r_i))^2 \right]^{1/2}. \quad (7)$$

For $H_2$, $N_2$, and $O_2$, the average error $\delta$ was 59.7 for $V_H$, 49.3 for $V_{LJ}$, 0.037 for $V_M$, 0.031 for $V_V$, 0.021 for $V_{HH}$, and 0.0044 for the hybrid $V$. The hybrid form $V$ is five times more accurate than the class-2 potentials and four orders of magnitude more accurate than the class-1 potentials.

Can $V(r)$ also represent weak noncovalent bonds? Using Gnuplot, we fitted $a$, $b$, $c$, and $e$ in Eq. (6) to Aziz’s accurate HFDID1 potential for Ar$_2$ and HFD-B po-
potential for Kr₂ [21] and set d equal to their London-tail coefficients. Figures 8–11 show that for 2 ≤ r ≤ 7 Å, the hybrid form [19] (solid, red) fits the Aziz potentials for both Ar₂ and for Kr₂ (pluses, blue). The Lennard-Jones LJ curves (dashes, green) matched at the minima are too deep for r > 4.5 Å (Figs. 7 & 10) and too hard for r < 3 Å (Figs. 9 & 10). The potential V(r) of Eq. (6) represents weak noncovalent bonds better than the L J (and H) of the hybrid form important in the liquid phase where more atoms interact, their potential energy is not the sum of the three (or more) pair potentials. Is the accuracy of the hybrid form important in the liquid phase where additivity is only approximate?

To test whether the lack of complete additivity in the liquid phase obscures the advantages of the hybrid form V over the Lennard-Jones potential V_LJ, we used both to compute the heats of vaporization ∆_vap H of Ar and Kr at their boiling points at atmospheric pressure. In our Monte Carlo simulations, we imposed periodic boundary conditions to reduce finite-size effects. Our Monte Carlo code is available at bio.phys.unm.edu/latentHeat. We used it to compute the potential energy U per atom in the liquid and gas phases. The latent heat of vaporization ∆_vap H is the difference between the potential energies U_gas and U_liquid plus the work done in expanding by ∆V against the pressure p of the atmosphere, ∆_vap H = U_gas − U_liquid + p ∆V.

The hybrid form V fitted to the curves of Figs. 7–10 gave ∆_vap H = 0.0694 eV (per atom) for Ar and 0.0982 eV for Kr, which differ from the experimental values [22] of 0.0666 and 0.0941 eV by 4.2% and 4.4%. In equivalent Monte Carlo simulations, the Lennard-Jones potential V_LJ fitted to r₀ and V(r₀) gave and ∆_vap H = 0.0787 eV for Ar and 0.111 eV for Kr (errors of 18% and 18%). So the errors due to a lack of additivity are of the order of 4%, while those due to the Lennard-Jones potential are about 18%. Even in the liquid phase, limited additivity is less of a problem than the defects of the Lennard-Jones potential.

For a wide class of atom pairs, the hybrid form can reliably represent the best spectroscopically determined potentials over all relevant distance scales. It also yields accurate second virial coefficients and heats of vaporization. Its simplicity recommends it as a teaching tool and as a practical form for computation. Given the differences between it and the Lennard-Jones, harmonic, Morse, Varnshi, and Hubert-Hirschfelder potentials, it would be worthwhile to examine the consequences of these differences in Monte Carlo searches for low-energy states of biomolecules and in numerical simulations of phase transitions and reactions far from equilibrium.

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