Early in our academic careers we learn that helium is an "inert gas" or, in more fashionable jargon, a "noble gas". The proximate explanation is that the 1s\(^2\) electronic configuration of the helium atom forms a closed shell, which lacks any immediate tendency to gain or lose electrons. Molecular orbital (MO) theory invites us to imagine a hypothetical He\(_2^+\) molecule with 4 electrons. The first two electrons go into the 1\(\sigma\)\(_g\) (or 1s\(\sigma\)) bonding MO but the third and fourth electron are relegated to 1\(\sigma\)\(_u\) (or 1s\(\sigma^*\)), which is an antibonding MO. Since the antibonding effect predominates slightly, it is predicted that He\(_2^+\) cannot exist as a stable molecule in its ground state. MO theory does however predict a bound He\(_2^+\) ion when one of the antibonding electrons is removed. This species has a transient existence of about 10\(^{-8}\) s, until it makes a transition to its unstable ground state.

Two helium atoms can attract weakly via van der Waals or London dispersion forces. This effect is generally pictured as an interaction between fluctuating electric dipoles of the two atoms caused by instantaneous deviations of their electron clouds from perfect spherical symmetry. A standard exercise in perturbation theory shows a long range attractive force as an interaction between fluctuating electric dipoles of the molecule. This effect is generally pictured as an interaction between fluctuating electric dipoles of the two atoms caused by instantaneous deviations of their electron clouds from perfect spherical symmetry. Theoretical studies of helium dimers date back to Slater (3) in 1928, who estimated a van der Waals binding energy of 8.9 K. Energies of this magnitude are conveniently expressed in temperature units, after dividing by Boltzmann’s constant, \(k_B\). On this scale, 1 K is equivalent to 1.98721 \times 10\(^{-3}\) kJ/mol, 8.61734 \times 10\(^{-5}\) eV, or 3.16682 \times 10\(^{-6}\) hartrees (atomic units). More recently, the He–He interaction potential has been accurately mapped from a combination of experimental data and ab initio computations. Aziz and coworkers (4) have constructed a semiempirical potential function based on scattering data, transport properties, and virial coefficients. Quantum Monte Carlo (QMC) computations by Anderson and coworkers (5) are in essential agreement with the semiempirical results. Monte Carlo methods refer to a class of computational algorithms that makes use of sequences of random numbers. These are particularly applicable in evaluating complicated many-electron integrals that occur in molecular computations. In principle, QMC methods are capable of determining numerically exact ground-state energies and wavefunctions.

The He–He potential is predicted to have a minimum of 10.9 K at a nuclear separation of 5.61 bohrs (2.97 Å). The semiempirical Aziz potential, specifically what is designated the LM2M2 analytic representation, is drawn in Figure 1. By way of comparison the H\(_2\) molecule has a well depth of 4.75 eV or 458 kJ/mol, larger by a factor of 5000. The H\(_2\) potential well can support just a single bound rotational–vibrational state (\(v = 0, J = 0\)) with an energy of approximately -1.176 mK. The dissociation energy of the molecule in its only rotational–vibrational state is smaller than the potential well.

Noble gas atoms at sufficiently low temperatures have long been known to form weakly-bound dimers and larger clusters bound by van der Waals forces. The long-sought \(^4\)He\(_2\) dimer was first definitively identified by Gentry and coworkers (1) in 1993, using electron-impact ionization on a high-pressure pulsed beam of helium with translational temperature as low as 0.3 mK (0.0003 K). Schöllkopf and Toennies (2) in 1994 detected the dimers by diffraction of a beam of helium atoms from a 200-nm silicon nitride transmission grating. \(N\)-atom helium clusters with nearly uniform beam velocity, \(v\), have de Broglie wavelengths given by

\[
\lambda = \frac{h}{Nmv}
\]

where \(h\) is Planck’s constant and \(m\) is the mass of a helium atom. For a beam normally incident on a grating, the diffraction angles \(\theta\) are determined by Fraunhofer’s formula

\[
N\lambda = d\sin\theta
\]

where \(N\) is the diffraction order and \(d\) the grating period. The diffracted beams were detected using an appropriately positioned mass spectrometer. Schöllkopf and Toennies were able to identify de Broglie waves corresponding to \(^4\)He\(_2\) dimers, as well as \(^4\)He\(_3\) trimers. 

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Figure 1. Aziz semiempirical helium interatomic potential \(V(r)\) (4). Points computed by Anderson (5) are shown as circles. The vertical axis is scaled as the function \(\text{sgn}(V) \ln(1 + |V|)\). A more conventional plot of \(V(r)\) on a linear scale is shown in Figure 2.
depth by a factor of about $10^4$. The bound state is just barely below the dissociation continuum threshold. The binding between two He atoms is so weak that even rotational excitation will result in dissociation. Moreover, the slightly lighter isotopomers $^3$He$^4$He and $^3$He$^3$He are both predicted to be unstable. The mean internuclear distance for $^4$He$_2$ is calculated to be $r = 54.6 \text{ Å}$, with an rms half-width $\sigma = \pm 48 \text{ Å}$. This would make $^4$He$_2$ the largest known diatomic molecule, as well as the most weakly bound. Gentry (6) has also confirmed this immense size by transmission of helium beams through nanoscale sieves of varying size. The interatomic potential and radial distribution function are sketched in Figure 2. Recall that the radial distribution function $D(r)$ describes the probability that two atoms are separated by a distance $r$, independent of their relative orientation. The helium dimer’s diameter is comparable to that of a small protein molecule, such as hemoglobin ($\sim 50 \text{ Å}$). By comparison, the internuclear distance in the H$_2$ molecule equals $0.74 \pm 0.15 \text{ Å}$.

For helium atoms interacting over such large distances, retardation effects, attributed to the finite speed of propagation of electromagnetic fields, must be included in the theoretical analysis. Casimir and Polder (7) worked out quantum-electrodynamic corrections for long-range intermolecular forces. They found that the $r^6$ asymptotic dependence for van der Waals interactions eventually approaches $r^7$ as $r \to \infty$. Gentry (8) estimated that the effects of retardation increases the energy of the ground state from $-1.310$ to $-1.176 \text{ mK}$.

It is well known that cooling by Joule–Thomson expansion is particularly effective in gaseous helium (below the Joule–Thomson inversion temperature of 40 K). This is due, in part, to an effect described by Wigner (9), whereby an energy level close to the threshold leads to a very large scattering cross-section. This allows the collision rate to remain high even at low densities. Dissociation of every dimer molecule in a collision is done at the expense of translational kinetic energy, so that reduction in kinetic energy results in further cooling of the expanding beam of gaseous helium.

**Quantum-Mechanical Model**

Within the Born–Oppenheimer approximation, the vibration of a diatomic molecule with an interatomic potential $V(r)$ is represented by the Schrödinger equation (10):

$$\left\{ -\frac{\hbar^2}{2\mu} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] - \frac{J(J+1)}{r^2} \right\} \psi_{v,J}(r) = E_{v,J} \psi_{v,J}(r) \quad (3)$$

We will use atomic units, in which $\hbar = m_e = 1$, and limit consideration to the lowest vibrational and rotational states, with $v = 0$ and $J = 0$. The reduced mass $\mu$ of a diatomic molecules is defined by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad (4)$$

where $m_1$ and $m_2$ are the masses of the separated atoms. We will be considering molecules made of $^4$He and $^3$He, for which the masses in atomic units (relative to the electron mass $m_e = 1$) are $m(^4\text{He}) = 7296.29$ and $m(^3\text{He}) = 5497.88$. The relevant reduced masses are

$$\mu_{34} = 3648.15, \quad \mu_{33} = 3135.34, \quad \mu_{34} = 2748.94 \quad (5)$$

The present authors have suggested a highly simplified model for helium dimers that reproduces their essential features without the need for elaborate computations (11). The interatomic potential is idealized as an attractive “Dirac bubble potential” of the form

$$V(r) = -\frac{\lambda}{2\mu^\gamma} \delta(r - \gamma) \quad (6)$$

A delta function represents the ultimate of a function limited to a single point. A well-known representation is the limit of a normalized Gaussian as the standard deviation $\sigma$ approaches zero:

$$\delta(r - \gamma) = \lim_{\sigma \to 0} \frac{1}{\sqrt{2\pi} \sigma} e^{-\frac{(r - \gamma)^2}{2\sigma^2}}$$

(Extreme specialization in graduate education has been likened to a delta function, whereby students are learning more and more about less and less until they ultimately know everything about nothing!)

A delta function potential might not seem, at first glance, to be a very useful approximation for the helium interatomic potential. However, the great disparity between the depth of the potential well and the minute binding energy of the ground state provides a convincing rationale for such an idealization.

For our more intrepid readers, the details of our computation are given in Appendix 1 in the Supplemental Material. The accurate QMC results can be fitted to the deltafunction...
model with the parameters $\lambda = 1.0701$, $r_0 = 13.15$ bohr (6.96 Å). The condition for a bound state, $\lambda > 1$, is just barely fulfilled. For $^3\text{He}^4\text{He}$ and $^3\text{He}_2$, the reduced masses listed in eq 5 imply values of $\lambda < 1$, consistent with the failure to observe either of these species.

**Helium Trimers**

In view of the extremely feeble bonding in $^3\text{He}_2$, it might appear unlikely that more than two helium atoms are able to form a stable species. In fact, however, this does happen! An apt analogy is the connection between Borromean rings, named after a noble Italian family during the Renaissance who used such a figure on their coat of arms. As shown in Figure 3, the three rings are interlocked in such a way that removal of any one causes the other two to fall apart.

A classic example of Borromean bonding involves the stability of some very important nuclei. Two alpha particles ($^4\text{He}$ nuclei) can have a fleeting association as an unstable $^8\text{Be}$ nucleus, with a half life of the order of $10^{16}$ s. But three alpha particles can form the stable $^{13}\text{C}$ nucleus and four can form $^{16}\text{O}$, otherwise you would not be reading this article! A macrocyclic molecule having the topology of Borromean rings has recently been synthesized (12).

The trimer species $^4\text{He}_3$ has been identified experimentally and its stability confirmed by theoretical analysis (13). A trimer ground state of approximately $-126$ mK is calculated and even an excited state of energy about $-2.24$ mK is predicted. A stable trimer $^3\text{He}^4\text{He}_2$ with an energy of $-11.4$ mK is also predicted.

We have suggested that the enhanced three-body bonding is a quantum-mechanical effect involving relative kinetic-energy operators (14). When the Schrödinger equation for the three-body system is written in terms of the relative particle coordinates $r_{12}$, $r_{23}$, and $r_{31}$, it contains operators of the form

$$-\frac{1}{2\mu} \left( \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} \right) + \text{analogys with } r_{23}, r_{31}$$

These are simple transcriptions of the relative kinetic energies of three classical particles. However, there also occur mixed second derivatives of the form $\frac{\partial^2}{\partial r_{12} \partial r_{23}}$, and so forth. The latter are of purely quantum origin, arising from the noncommutativity of the relative momentum operators $-\hbar \nabla_{12}, -\hbar \nabla_{23}$, and $-\hbar \nabla_{31}$.

We carried out a variational computation on the helium trimer, approximating the wavefunction by

$$\Psi(r_{12}, r_{23}, r_{31}) = \psi(r_{12}) \psi(r_{23}) \psi(r_{31})$$

where $\psi(r_0)$ has the analytic form of our dimer wavefunction. The computed energy of the trimer is $-96.1$ mK. Although this correctly predicts a trimer about two orders of magnitude more stable than the dimer, the quantitative result deviates significantly from the accurate ground-state energy of $-126$ mK. Still, analysis of individual energy contributions suggests the origin of the trimer’s relative stability. The mixed second derivatives contribute $-114$ mK to the trimer ground-state energy, sufficient to overcome a $+18$ mK destabilization from the pairwise-additive kinetic and potential energy contributions. Details of the trimer computation are given in Appendix 2 in the Supplemental Material.

Blume and Greene (16) have carried out QMC computations based on the adiabatic hyperspherical approximation for $^4\text{He}_N$ clusters, $N = 3$ to 10. Their results for the cluster ground-state energies are plotted in Figure 4. As $N \to \infty$, one would expect the binding energy per atom to approach a value consistent with $\lambda_{\text{opt}} H$ for helium, 84.5 J/mol at 4.216 K. The present authors have also developed a simplified model for these larger clusters (17). Information gained on the extreme low-temperature behavior of matter is relevant to current research on Bose–Einstein condensates.

**Figure 3.** Borromean rings in a well-known logo. (This does not constitute an endorsement of the product.)

**Figure 4.** Energies of $^4\text{He}_N$ clusters according to computations of Blume and Greene (16).
Supplemental Material

The deltafunction calculations for the helium dimer and variational computation on the helium trimer are available in this issue of JCE Online.

Literature Cited