Theoretical Foundations of Near-Contact Repulsion from Quantum Confinement

Asymptotic Structure, Boundary Justification, and Validation Framework

Keith Taylor VERSF Theoretical Physics Program

Plain Language Summary

What this paper is about: Our main paper showed that atoms push each other away when they get very close, following a simple mathematical rule — the repulsive force grows as one divided by the gap-distance squared ($1/g^2$). This paper answers the deeper question: *why should we believe that rule, and when exactly does it apply?*

The core idea in everyday terms: Imagine slowly closing a book on a rubber ball. As the pages press together, the ball gets squeezed into an increasingly narrow space. The harder you squeeze, the more the ball resists — and that resistance grows dramatically as the space gets very thin. Something similar happens to electrons when atoms approach each other. The electrons get trapped in the narrowing gap between atoms, and quantum mechanics tells us that confining anything to a smaller space always costs energy. That energy cost is what pushes the atoms apart.

What we prove here: We show that this "quantum squeezing" argument holds up under rigorous examination. Specifically:

- The electrons don't need to hit a literal wall — even a very steep barrier produces the same $1/g^2$ behavior at close range (like how a ball bouncing between two surfaces doesn't care whether the surfaces are made of steel or diamond, as long as they're hard enough).
- We only need to think about squeezing in one direction (straight between the two atoms) because that direction is so much more constrained than the others that it dominates the physics.
- The same mathematical formula works for all types of atoms — different elements just change the strength of the effect, not its fundamental character, much like gravity follows the same inverse-square law for all objects but the strength depends on their masses.
- We can test this theory: we describe four specific experiments or calculations that would prove us wrong if the theory is incorrect.

Why a companion paper? The main paper presents the formula and shows it works. This paper shows *why* it works — providing the mathematical justification that reviewers and fellow physicists need to trust the result. Think of the main paper as showing you a bridge and demonstrating that cars can drive across it; this paper is the engineering analysis showing why the bridge can bear the load.

Reading guide. Sections 2–4 provide the theoretical justification of the $1/g^2$ asymptotic. Section 5 addresses universality and element-dependent prefactors. Sections 6–8 define scope, crossover, and falsification protocols. The *"For the general reader"* paragraphs throughout can be skipped without loss of technical continuity.

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Abstract

This companion paper provides the theoretical foundations underlying the confinement-based near-contact repulsion law $V(g) \propto 1/g^2$ derived in the main paper [1]. Within the Born–Oppenheimer approximation [2, 3], electronic kinetic energy associated with transverse confinement in a narrowing internuclear gap contributes a repulsive term to the nuclear potential energy surface that diverges as $1/g^2$, where $g = r - r_0$ is the surface-to-surface separation. We demonstrate that this scaling is robust: one-dimensional confinement captures the leading three-dimensional physics because normal and transverse energy scales separate by a factor $R/g \gg 1$ near contact [4, 5], and hard-wall (Dirichlet) boundary conditions arise as asymptotic attractors of any sufficiently steep Pauli exclusion profile rather than requiring literal infinite barriers [6, 7]. Element-dependent prefactors enter as participation renormalization of a universal functional form, analogous to system-dependent coupling constants in other inverse-square force laws. We reconcile this asymptotic with empirical exponential cores [8], characterize the crossover regime, and establish a falsification framework with specific ab initio test protocols. This paper does not propose a replacement for quantum chemistry; it provides a physically grounded asymptotic constraint for the repulsive wall with minimal parameters, systematic corrections, and explicit scope.

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1. Introduction and Scope of Claims

1.1 The Asymptotic Gap in Repulsive Core Modeling

Short-range interatomic repulsion is conventionally represented by phenomenological exponential forms—most commonly the Born–Mayer potential $V(r) = A \cdot \exp(-r/\lambda)$ [8]—which reproduce ab initio repulsive walls adequately over finite distance ranges. These forms have two well-known limitations: they require system-specific parameterization (typically 2–5 free parameters per atom pair), and they lack a clear asymptotic justification in the near-contact limit.

The main paper [1] proposes that electronic confinement in a narrowing internuclear gap produces a leading repulsive contribution scaling as $V(g) \propto 1/g^2$, where $g = r - r_0$ is the gap between effective atomic boundaries. This companion paper provides the theoretical justification for that proposal.

For the general reader: When scientists simulate how atoms interact — to design drugs, predict material properties, or model chemical reactions — they need mathematical formulas describing the forces between atoms. The standard formulas for close-range repulsion were invented nearly a century ago and work reasonably well, but they're essentially educated guesses: you pick a mathematical shape and then adjust several numbers until it matches experimental data. Our main paper proposed a new formula grounded in fundamental physics rather than guesswork. This companion paper shows the rigorous reasoning behind it.

1.2 Precise Statement of Claim

We claim that as $g \to 0$, the repulsive wall admits a **confinement-dominated asymptotic form**:

$$V(g) = \chi\_AB \cdot (\hbar^2\pi^2) / (2m_e g^2) + \mathcal{O}(1/g)$$

where χ_AB is a dimensionless participation factor encoding valence electronic structure, and the subleading corrections arise from screening, curvature, and boundary softness.

We do **not** claim that all chemically relevant repulsion is exactly $1/g^2$ at all separations. We do **not** claim that exponential cores are incorrect—only that they are effective finite-range approximations to a deeper asymptotic structure. We do **not** claim that this framework replaces quantum chemistry or machine-learned potentials; it provides an asymptotic constraint that complements them.

For the general reader: We want to be very precise about what we're saying and what we're not saying. Our claim is that when atoms get *extremely* close together, the repulsive force follows a specific pattern ($1/g^2$). We're not saying this pattern applies everywhere or that existing methods are wrong — just that existing methods are approximations that happen to work well over the ranges where they've been tested, and our formula reveals what's actually happening at the deepest level of close approach.

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2. From Confinement Energy to Effective Interatomic Potential

2.1 Born–Oppenheimer Origin of the Repulsive Wall

Within the Born–Oppenheimer (BO) approximation [2, 3], electronic degrees of freedom adjust adiabatically to nuclear positions, and the electronic ground-state energy E_elec(**R**) defines the potential energy surface governing nuclear motion. All contributions to E_elec—including electronic kinetic energy—enter the nuclear Hamiltonian as effective potential terms.

As two atoms approach near contact, the electronic density in the overlap region is compressed into a narrowing gap of width g. The dominant contribution to the change in E_elec in this regime arises from **kinetic energy associated with transverse confinement**, which diverges as

$1/g^2$, and therefore dominates the repulsive wall in the near-contact limit over contributions that remain bounded or diverge more slowly with decreasing gap width.

This is not a new approximation. It is a direct consequence of the standard BO framework: electronic kinetic energy is part of E_elec, and confinement drives the kinetic term to dominate the repulsive wall at small g.

Comparison with exchange-repulsion scaling. A key question is whether confinement kinetic energy actually dominates over other contributions that also grow at short range — particularly exchange-repulsion, which scales with the square of the overlap integral between occupied orbitals. For exponentially decaying atomic wavefunctions with decay length κ, the overlap integral in the gap region scales as $\exp(-\kappa g)$, making the exchange contribution scale as $\exp(-2\kappa g)$. This grows steeply but remains finite as $g \to 0$: at complete superposition ($g = 0$) the overlap integral reaches its maximum value, bounded above by orbital normalization, and the exchange contribution correspondingly saturates to a finite ceiling. The confinement kinetic energy, by contrast, diverges as $1/g^2$. Any function that diverges algebraically eventually dominates over any function that saturates to a finite value, regardless of how steep the transient growth is. This separation of asymptotic behavior is what ensures that the confinement channel dominates the repulsive wall in the near-contact limit.

We emphasize, however, that at intermediate separations — where exchange, hybridization, and correlation all contribute comparably — the confinement term is not isolated and the full electronic structure must be considered. The participation factor χ_{AB} (Section 5) absorbs the net effect of these contributions at the boundary of the near-contact regime. In this sense, χ_{AB} encodes more physics than pure electron counting: it reflects the effective electronic participation as modified by exchange and correlation at the onset of the confinement-dominated regime.

For the general reader: A natural question arises: electrons are tiny particles zipping around inside atoms — how does their *motion energy* become a *force between atoms*? The answer lies in a nearly century-old simplification called the Born–Oppenheimer approximation, which is the foundation of almost all modern chemistry calculations. It works like this: electrons move so much faster than the heavy atomic nuclei that we can solve for what the electrons do at each fixed position of the nuclei, and then use the resulting energy as the "landscape" that the nuclei roll around on. Since the electrons' kinetic energy is part of that landscape, squeezing electrons into a tighter space (which increases their kinetic energy) shows up as a hill that pushes the nuclei apart. This isn't a new idea — it's a direct consequence of the standard framework that chemists and physicists have used successfully since the 1920s.

2.2 Leading-Order Confinement Scaling

Consider the electronic wavefunction component $\psi(z)$ normal to the interface between two approaching atoms, confined to a gap of width g. The lowest transverse eigenmode satisfies

$$-(\hbar^2/2m_e) \cdot d^2\psi/dz^2 = E_1 \cdot \psi(z)$$

with boundary conditions enforcing vanishing amplitude at the gap edges (justified in Section 4). The lowest eigenvalue is

$$E_1(g) = \hbar^2 \pi^2 / (2 m_e g^2)$$

As $g \to 0$, this term diverges faster than any competing contribution to E_elec, establishing $1/g^2$ as the leading asymptotic behavior of the repulsive wall.

Dimensional analysis cross-check. The confined electron problem contains three quantities: $\hbar$, m_e, and g. The unique energy scale constructable from these is $\hbar^2/(m_e g^2)$. No intrinsic length scale enters, which is why the resulting potential is scale-free—a point we return to in Section 6.

For the general reader: This is the mathematical heart of the argument, and it's essentially the "particle in a box" problem from introductory quantum mechanics. When you confine a quantum particle (here, an electron) between two walls separated by a distance g, the minimum energy it can have is proportional to $1/g^2$. Make the box half as wide, and the energy quadruples. This is a bedrock result of quantum mechanics — it's taught in every undergraduate physics course. The insight of this paper is recognizing that the gap between two approaching atoms *is* such a box, and the energy cost of confining electrons in that box is what drives the atoms apart. The dimensional analysis check confirms this is the only possible answer: given just the fundamental constants ($\hbar$, m_e) and the gap width (g), there is exactly one way to build an energy, and it's proportional to $1/g^2$.

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3. Why One-Dimensional Confinement Captures Three-Dimensional Physics

3.1 Energy Scale Separation Near Contact

Near contact, confinement is highly anisotropic. Motion normal to the interface (the gap direction) is restricted on a scale g, while motion parallel to the interface occurs over a lateral extent set by the local geometric mean of the gap width and the radius of curvature R of the facing surfaces [4, 5].

The resulting energy scales are:

E_normal $\sim \hbar^2 / (2 m_e g^2)$

E_tangential $\sim \hbar^2 / (2 m_e R g)$

so that

E_normal / E_tangential $\sim R/g \gg 1$ as $g \to 0$

For typical atomic radii R ~ 1–2 Å and near-contact gaps g < 0.3 Å, this ratio exceeds 3–6, ensuring that the normal (gap-direction) confinement mode dominates.

For the general reader: A reasonable objection is: "Atoms exist in three dimensions, but you're using a one-dimensional model. Isn't that too simple?" The answer is no, and here's why. Imagine squeezing a water balloon between your hands. The balloon is being compressed in one direction (between your palms) but can still bulge outward in the other two directions. The squeezing direction is where all the action is — that's where the pressure builds up most intensely. The same thing happens with electrons between two approaching atoms. The gap is extremely narrow in one direction but relatively wide in the other two. The energy cost of being squeezed in the narrow direction is several times larger than the cost of the gentle confinement in the wide directions, and this ratio grows as R/g as the gap shrinks — meaning the narrow direction becomes ever more dominant as atoms approach contact.

3.2 Controlled Corrections from Transverse Modes

Transverse modes contribute corrections suppressed by powers of g/R. The first such correction modifies the effective potential as

$$V(g) = [\hbar^2\pi^2 / (2m_e g^2)] \cdot [1 + \mathcal{O}(g/R)]$$

which can be absorbed into the curvature correction terms of the main paper [1]. The one-dimensional model is therefore not an approximation of convenience but a controlled leading-order description with a quantified error bound.

For the general reader: The "other two directions" don't just disappear — they contribute small corrections that we can calculate and account for systematically. This is important because it means the one-dimensional model isn't a rough guess; it's a precise leading approximation with a known, small error that we can improve upon when needed.

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4. Dirichlet Boundaries as Asymptotic Attractors

4.1 The Boundary Condition Question

The derivation in Section 2.2 assumes Dirichlet (hard-wall) boundary conditions: $\psi(0) = \psi(g) = 0$. Since Pauli exclusion produces a steep but smooth repulsive barrier—not a literal infinite wall—the physical validity of this assumption requires justification.

The key result, established in the mathematical physics literature [6, 7, 9], is that hard-wall eigenvalues are **asymptotic attractors** of the low-lying spectrum for any sufficiently steep confining potential, provided the penetration depth δ satisfies $\delta \ll g$.

For the general reader: This section addresses perhaps the most important challenge to our theory. In Section 2, we treated the edges of the gap as perfectly rigid walls that electrons can't penetrate at all. But in reality, the barriers aren't perfect walls — they're more like very steep hills. Electrons can "leak" slightly into these hills (a quantum phenomenon called tunneling). So the critical question is: does this leakage ruin our $1/g^2$ result? The answer, proven by mathematicians decades ago, is no. As long as the hills are steep enough compared to the gap width, the mathematics produces essentially the same answer as if the walls were perfectly rigid. The steeper the hill and the wider the gap, the closer the agreement. This is why we call hard walls "asymptotic attractors" — any sufficiently steep barrier naturally produces the hard-wall result as its limiting behavior.

4.2 Quantitative Convergence

Consider a steep confining potential near each boundary that produces an evanescent penetration depth δ. In the regime $\delta/g \ll 1$, the lowest eigenvalue is well-approximated by the hard-wall form with an effective gap $g\_eff = g - 2\delta$ [6]:

$$E_1(g) \approx [\hbar^2\pi^2 / (2m_e(g - 2\delta)^2)] \cdot [1 + \mathcal{O}(\delta/g)]$$

The leading divergence remains $1/g^2$, with boundary softness producing two effects:

1. **Gap renormalization**: the effective gap width shifts from g to $g\_eff = g - 2\delta$, absorbed into a redefinition of r_0.
2. **Subleading corrections**: terms of order δ/g contribute to the $1/g$ correction tier.

In practice, the hard-wall approximation is justified when the evanescent penetration depth into the exclusion region is small compared to the geometric gap, $\delta/g \ll 1$. In that regime, boundary softness primarily renormalizes the effective gap width $g\_eff = g - 2\delta$, while the leading divergence remains $1/g^2$. When δ/g is not small, the appropriate description is a soft-wall or Robin-boundary formulation, which maps naturally onto the $1/g$ correction tier discussed in Section 7.

For the general reader: What happens quantitatively when the walls aren't perfectly rigid? Two things. First, the effective gap becomes slightly narrower — instead of the full geometric gap g, the electrons "see" a gap of g minus a small correction on each side (the penetration depth δ). This is like measuring the usable space inside a room by accounting for thick, padded walls — the room is a bit smaller than the outer dimensions suggest. Second, there are small additional corrections proportional to δ/g. Both effects are naturally handled by our correction framework (Section 7). The crucial point is that the fundamental $1/g^2$ behavior survives intact.

4.3 Connection to WKB and Semiclassical Methods

This convergence is a standard result in semiclassical quantum mechanics [11, §50]. In the WKB framework, a steeply rising potential produces a turning point that effectively acts as a hard wall for the low-lying modes, with corrections controlled by the barrier steepness and penetration

depth. The Dirichlet limit corresponds to the regime where the exclusion barrier is steep compared to the low-lying confined mode energy—precisely the situation at small g.

For the general reader: The WKB method is a well-established technique for connecting quantum and classical physics — it's been a standard tool since the 1920s. It confirms our argument from a completely different mathematical direction: when a barrier is much taller than the energy of the particle bouncing off it, the barrier acts like a rigid wall for all practical purposes. Between two approaching atoms, the Pauli exclusion barrier is enormously tall compared to the confinement energy we're calculating, so the rigid-wall approximation is well justified.

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5. Universality, Prefactor Renormalization, and χ_AB

5.1 What "Universal" Means Here

Universality refers to the **functional form** of the leading asymptotic: $V(g) \propto 1/g^2$. This scaling follows from dimensional analysis and the structure of the confinement eigenvalue problem, independent of atomic species, electronic configuration, or temperature.

The **amplitude** of the divergence is not universal. It depends on how many electrons participate in confinement and how effectively they are confined. This is standard in physics: gravitational and Coulomb forces share a universal $1/r^2$ form with system-dependent coupling constants ($G m_1 m_2$ and $k q_1 q_2$ respectively). Universal functional form with system-dependent amplitude is not a contradiction—it is the norm for fundamental force laws.

For the general reader: When we say this law is "universal," we mean the *pattern* ($1/g^2$) is the same for all atoms — but the *strength* varies from element to element. This is exactly how gravity works: every object in the universe attracts every other object following the same $1/r^2$ pattern, but heavier objects pull harder. Nobody would say gravity isn't universal just because Jupiter pulls harder than Earth. Similarly, carbon atoms resist being squeezed together more strongly than helium atoms, but both follow the same $1/g^2$ law. The strength difference is captured by a single number for each pair of elements, called χ_AB.

5.2 Physical Content of χ_AB

The participation factor χ_AB encodes the fraction of electronic density that contributes to confinement energy in the gap region. Its physical content includes:

- **Valence participation**: Core electrons, tightly bound to their nuclei, contribute negligibly to the overlap region. χ_AB scales approximately with effective valence electron count.
- **Polarizability effects**: More polarizable atoms have more diffuse valence density, modifying the effective density in the gap. This motivates the scaling χ_AB $\propto$ $(\alpha\_ref/\alpha\_AB)^{(2/3)} \cdot Z\_val$ used in the main paper [1].

- **Orbital character**: The angular momentum structure of the participating orbitals affects the transverse mode structure, contributing to χ_AB at the 10–20% level.

Critically, χ_AB does not modify the functional form of the repulsion—it multiplies the universal $1/g^2$ divergence by a dimensionless constant that can be estimated from tabulated atomic properties [12, 13] or extracted from a single ab initio calculation per element. This is participation renormalization, not ad hoc fitting.

For the general reader: What determines how strong the repulsion is for a given pair of atoms? Mainly, how many electrons are available to be squeezed into the gap. Atoms have two types of electrons: "core" electrons that are tightly locked near the nucleus and don't really participate, and "valence" electrons (the outer ones involved in chemical bonding) that are the ones getting squeezed. An atom like carbon, with 4 valence electrons, produces stronger confinement repulsion than hydrogen with just 1. The factor χ_AB captures this — and the key advantage is that it can be estimated from known atomic properties, without needing to run expensive computer simulations for every pair of atoms.

5.3 Bounds on χ_AB

Physical constraints limit χ_AB to a finite range. For a system with Z_val participating valence electrons:

- **Lower bound**: $\chi\_AB > 0$ (nonzero participation).
- **Upper bound**: $\chi\_AB \leq Z\_val,A + Z\_val,B$ (all valence electrons confined).
- **Typical values**: For closed-shell noble gas pairs, where only diffuse outer electrons participate, χ_AB is expected in the range ~0.5–2. For open-shell main-group pairs (e.g., C–C, N–N, O–O) with multiple valence electrons available for confinement, $\chi\_AB \approx 2$–8. Values approaching the upper bound would indicate nearly complete valence participation and are expected only for highly compressed, electron-rich pairs.

These bounds provide an internal consistency check: extracted values of χ_AB falling outside this range would signal a breakdown of the confinement picture.

For the general reader: Because χ_AB has a clear physical meaning (how many electrons participate), we can set limits on what values make sense. If a calculation ever returned a negative χ_AB, or one larger than the total number of valence electrons, we'd know something was wrong with the model. This kind of built-in sanity check is an advantage over purely empirical formulas, where the fitting parameters have no physical meaning and therefore no natural bounds.

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6. Power-Law vs. Exponential: Reconciliation and Crossover

6.1 Why Exponentials Work Over Finite Ranges

Empirical repulsive cores are commonly written as $V(r) = A \cdot \exp(-r/\lambda)$, where λ is a characteristic decay length reflecting the exponential falloff of electron density at large distances from the nucleus [8, 14]. This length scale is physically meaningful: it encodes the spatial extent of the outermost occupied orbitals.

In the gap coordinate $g = r - r_0$, the exponential form becomes $V(g) = A' \cdot \exp(-g/\lambda)$, which approaches a finite value A' as $g \to 0$. The confinement asymptotic, by contrast, diverges as $1/g^2$. These cannot both be correct globally—but they need not be.

Over a finite fitting window $g \in [g\_min, g\_max]$, an exponential can approximate a power law to within typical fitting tolerances. The exponential's success as a phenomenological form is not evidence against the confinement asymptotic; it reflects the practical reality that most calibration data samples the intermediate regime rather than the extreme near-contact limit.

For the general reader: Scientists have used exponential formulas for atomic repulsion for nearly a century, and they work well in practice. So why change? The issue is subtle: exponential formulas approach a fixed ceiling as atoms get arbitrarily close, while our confinement formula grows without limit. Over the range where experiments have been done, both formulas look similar enough that either one fits the data. But they make very different predictions at extreme close range — and our formula is the one grounded in fundamental physics. This is analogous to how Newton's gravity works perfectly for everyday situations but Einstein's general relativity is needed for extreme conditions near black holes. The exponential formulas are the "Newtonian" description; the confinement formula reveals the deeper structure.

6.2 Crossover Regime

The crossover gap g^* can be defined operationally as the separation at which the confinement contribution C_2/g^2 becomes comparable to a chosen phenomenological representation of the repulsive wall (e.g., an exponential core fit over a specified window). Equating $C_2/g^2 \sim A' \cdot \exp(-g/\lambda)$ yields a system- and definition-dependent crossover that separates a near-contact asymptotic regime from an intermediate fitting regime.

Below g^*, the confinement term dominates and the $1/g^2$ scaling should be directly observable in sufficiently resolved data. Above g^*, exponential forms remain adequate representations. The confinement framework suggests interpreting the phenomenological decay length λ as encoding boundary-softness and orbital-extent effects that enter the confinement framework through an effective penetration depth δ (Section 4.2) and related subleading corrections. Determining g^* empirically for specific systems is a central goal of the ab initio discrimination protocol described in Section 8.2.

Order-of-magnitude estimate for He–He. For the helium dimer, the Born–Mayer parameters are approximately $A' \approx 20$ eV and $\lambda \approx 0.2$ Å [8, 16], while $C_2 = \hbar^2\pi^2/(2m_e) \approx 3.81$ eV·Å² with $\chi\_AB \approx 1$ for two closed-shell atoms with minimal valence participation. Equating $C_2/g^2 = A' \cdot \exp(-g/\lambda)$ and solving numerically yields $g^* \approx 0.3$–0.4 Å. This is well above the regime where nuclear size effects or relativistic corrections become relevant ($g \lesssim 0.01$ Å), confirming that the $1/g^2$ regime is physically accessible for this system. For heavier atoms with more diffuse

electron densities, g* is expected to be comparable or larger. If g* were found to be below ~0.05 Å for all systems, the confinement regime would be physically inaccessible and the framework would lose practical relevance — this constitutes an additional implicit falsifiability condition.

For the general reader: There's a transition zone — a gap distance we call g* — where the physics shifts from the regime where exponential formulas work well to the regime where confinement dominates. Think of it like water in a river: far upstream, the water flows smoothly and you can describe it with simple equations; near a waterfall, turbulence takes over and you need different physics. The exact location of g* depends on the specific atoms involved, and determining it through computation and experiment is one of the key next steps for this research program.

6.3 Dimensional Analysis as Consistency Check

The confined-electron problem in the gap contains three fundamental quantities: $\hbar$, m_e, and g. No combination of these produces a length scale—the problem is intrinsically scale-free. Any intrinsic length (such as the exponential's λ) must enter through boundary corrections or environmental effects, confirming that the leading asymptotic is necessarily a pure power law. The exponent -2 follows from the requirement that V(g) has dimensions of energy.

We emphasize that this argument confirms the internal consistency of the confinement model rather than independently establishing the $1/g^2$ asymptotic. The actual physical problem contains additional scales — nuclear charges, orbital radii, screening lengths — that could in principle modify the asymptotic. The reduction to a pure confinement problem, in which these additional scales enter only through subleading corrections and the prefactor χ_AB, rests on the physical arguments of Sections 2–4 (dominance of confinement kinetic energy, energy scale separation, Dirichlet attractor convergence). Dimensional analysis then guarantees that if the confinement picture is correct, the leading term must take the $1/g^2$ form — but it does not by itself prove that the confinement picture applies.

For the general reader: This is a powerful argument from dimensional analysis — a technique that physicists use to constrain answers before doing any detailed calculation. The confinement problem involves only three ingredients: Planck's constant ($\hbar$), the electron mass (m_e), and the gap width (g). There is exactly one way to combine these into an energy, and it gives $1/g^2$. There's no room for an exponential to appear because there's no built-in length scale to put in the exponent. Any length scale (like the λ in the exponential formula) must come from outside the core confinement problem — from the shape of the boundaries or the electronic environment. This is why we say the confinement law is "scale-free": it contains no arbitrary lengths that need to be fitted. An important caveat: dimensional analysis tells us the answer *if* the confinement picture is correct — the earlier sections of this paper establish *that* it is correct.

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7. Systematic Corrections: Organization and Physical Origin

7.1 Correction Hierarchy

Beyond the leading $1/g^2$ term, the complete near-contact potential admits the expansion:

$$V(g) = C_2/g^2 + C_1/g + C\_H \cdot H/g + \mathcal{O}(1)$$

where $C_2 = \chi\_AB \cdot \hbar^2\pi^2/(2m_e)$, and the subleading terms have distinct physical origins.

For the general reader: The $1/g^2$ term is the dominant effect, but it's not the whole story. Real atoms aren't featureless spheres in a vacuum — they have curved surfaces, they may be surrounded by other atoms (in a metal or crystal), and their boundaries aren't perfectly rigid. Each of these real-world complications adds a smaller correction term to the formula. The key advantage of our approach is that these corrections arise naturally from the physics rather than being added as arbitrary adjustments. We know *why* each correction exists and *how* it should behave, which makes the model far more predictable than one built from empirical fitting alone.

7.2 Screening Correction (C_1/g)

In condensed phases, electronic screening modifies the effective boundary conditions from pure Dirichlet to Robin-type ($\alpha \cdot \psi + \beta \cdot \partial\psi/\partial n = 0$) [17]. The leading eigenvalue correction from Robin boundaries scales as $1/g$, with amplitude set by the screening environment:

- **Metallic systems**: C_1 scales with the Thomas–Fermi screening length λ_TF [18].
- **Insulating systems**: C_1 scales with the dielectric screening length.
- **Vacuum**: $C_1 \to 0$, recovering the pure Dirichlet limit.

This provides a testable prediction: force–distance curves for identical atom pairs should differ measurably between metallic and insulating environments, with the difference scaling as $1/g$.

For the general reader: When atoms are surrounded by other atoms (as in a solid material), the surrounding electrons partially shield or "screen" the confinement effect. In a metal, where electrons flow freely, this screening is stronger than in an insulator like glass. This means the repulsion between two identical atoms should measurably differ depending on whether they're in a metallic or insulating environment. This is a concrete, testable prediction that distinguishes our framework from purely empirical approaches.

7.3 Curvature Correction ($C\_H \cdot H/g$)

For curved atomic surfaces with mean curvature $H = \frac{1}{2}(1/R_1 + 1/R_2)$, thin-domain eigenvalue asymptotics yield a correction of order H/g [4, 5]. Since this has the same $1/g$ dependence as the screening term, the two must be distinguished by their scaling with geometry:

- **Screening**: Independent of surface curvature; depends on electronic environment.
- **Curvature**: Scales with H; independent of electronic environment at leading order.

Experimentally, varying tip radius in AFM measurements while holding the electronic environment constant isolates the curvature contribution; varying the substrate (metallic vs. insulating) while holding the geometry constant isolates the screening contribution.

For the general reader: Atoms aren't flat — they're roughly spherical, and the curvature of their surfaces affects the confinement. A sharply curved surface (a small atom) produces a different correction than a gently curved one (a large atom). Both the screening and curvature effects produce corrections of similar mathematical form ($1/g$), but they respond to different experimental knobs: curvature depends on geometry while screening depends on the electronic environment. By varying one while holding the other fixed, experimenters can separately measure each contribution.

7.4 Boundary Softness Correction

Finite penetration depth δ modifies the leading term through gap renormalization (Section 4.2), contributing effective corrections at order δ/g^2 which can be absorbed into a redefined r_0 or treated as a systematic uncertainty.

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8. Validation Framework

For the general reader: This section is about intellectual honesty. Any good scientific theory must be testable — it must make predictions that could be proven wrong. Here we lay out exactly what we predict, how to test it, and what results would force us to abandon the theory. We also carefully distinguish between cases where we fitted our formula to data (calibration), applied it to new situations (transfer), and made genuinely blind predictions.

8.1 Epistemic Hierarchy

We distinguish four levels of empirical engagement, in order of increasing evidential strength:

Level	Definition	Example
Calibration	Parameters adjusted to reproduce target data	Fitting C_2, r_0 to H_2 dimer
Transfer	Calibrated parameters applied to new systems	H_2 parameters predicting D_2 properties
Prediction	All parameters from external sources	Tabulated radii + universal C_2 predicting noble gas dimers
Falsification	Data that would refute the model	Ab initio log–log slopes $\neq -2$ at small g

Claims in the main paper [1] are labeled according to this hierarchy. No calibrated result is presented as a prediction.

For the general reader: Scientists sometimes blur the line between "fitting" (adjusting a formula to match known data) and "predicting" (using a formula to forecast unknown results). Fitting is easy — almost any formula with enough adjustable numbers can be made to fit known data. Prediction is hard and is the true test of understanding. We're very careful to label which of our

results are fits, which are transfers to new systems, and which are genuine predictions. This transparency lets readers judge the strength of evidence for themselves.

8.2 Specific Falsification Protocols

The confinement model makes the following testable claims, each of which could decisively falsify the framework:

Protocol 1: Ab initio slope test. Compute CCSD(T)/aug-cc-pVQZ [19, 20] (or comparable) potential energy curves for:

- Noble gas dimers: He–He, Ne–Ne, Ar–Ar
- Covalent pairs: H_2, N_2, O_2
- Mixed pairs: He–Ne, Ar–Kr

Convert to gap coordinates $g = r - r_0$ using tabulated van der Waals radii [12]. Plot log V vs. log g in the repulsive wall region ($g < 0.5$ Å).

Prediction: Local slope approaches -2 as $g \rightarrow 0$. *Falsification*: Slopes converge to a value distinguishable from -2 (e.g., -1.5 or -3) at the 95% confidence level across multiple systems.

In practice, the repulsive wall can be isolated either by fitting only sufficiently short separations where attraction is negligible or by subtracting a reference dispersion model (e.g., DFT-D3 or Tang–Toennies [27]) consistently across systems.

Sensitivity to r_0 choice. The gap coordinate $g = r - r_0$ requires specifying the contact distance r_0, which is not uniquely defined: van der Waals radii, covalent radii, and electron density isosurface radii can differ by 0.2–0.5 Å for the same element pair [12]. Since the log-log slope $d(\log V)/d(\log g)$ depends on the coordinate origin, the extracted exponent is sensitive to r_0. This sensitivity can be assessed by repeating the slope extraction across a range of r_0 values spanning ± 0.2 Å around the nominal van der Waals sum. If the confinement asymptotic is genuine, there should exist a well-defined r_0 value at which the slope converges to -2, and the convergence should be robust: the extracted slope should remain within the range -2 ± 0.3 for all r_0 choices within ± 0.15 Å of the optimal value. If instead the apparent slope of -2 can only be obtained by fine-tuning r_0 to implausible precision (< 0.01 Å), this would weaken the claim. The r_0 sensitivity test is therefore an integral part of Protocol 1, not a separate validation step.

For the general reader: This is the most direct test. Using the most accurate quantum chemistry methods available (called CCSD(T), the "gold standard" of computational chemistry), we can calculate the repulsive energy between pairs of atoms at very close range. If our theory is correct, plotting this energy on a log-log graph should give a straight line with a slope of exactly -2. If the slope is consistently different from -2 — say, -1.5 or -3 — then our theory is wrong. This test can be performed today with existing software.

Protocol 2: Force–distance scaling. Measure AFM or SFA force–distance curves at sub-ångström resolution on well-characterized flat surfaces [15, 16, 28].

Prediction: Force scales as $F(g) \propto 1/g^3$ in the near-contact regime ($g < g^* \approx 0.3$ Å). *Falsification*: Force saturates or follows a qualitatively different scaling below g^*.

For the general reader: Atomic force microscopes (AFMs) can directly measure the force between a tiny tip and a surface as they're brought together. Our theory predicts that this force should grow as $1/g^3$ (the derivative of the $1/g^2$ energy) at very close range. If instead the force levels off or follows a different pattern, our theory would be falsified. This is a direct experimental test using instruments that already exist in many laboratories worldwide.

Protocol 3: Temperature independence. Measure the repulsive wall parameters C_2 and r_0 at temperatures spanning 100–1000 K.

Prediction: Both parameters are temperature-invariant to within experimental uncertainty, since confinement is a ground-state electronic property. *Falsification*: Systematic temperature dependence of C_2 exceeding 5%.

For the general reader: Since the confinement effect comes from the fundamental quantum behavior of electrons (not from thermal motion or vibration), our formula's key numbers should not change with temperature. If you measure atomic repulsion at room temperature and at 1000 K, you should get the same result. If the numbers shift significantly with temperature, something else is going on that our model doesn't capture.

Protocol 4: Curvature systematics. Compare force–distance curves for AFM tips of varying radius R on the same substrate [21].

Prediction: The $1/g$ correction scales linearly with mean curvature $H \propto 1/R$. *Falsification*: Curvature correction absent or scaling nonlinearly with $1/R$.

For the general reader: By using AFM tips of different sharpness (different radii) on the same surface, experimenters can test whether the curvature correction behaves as our theory predicts. Sharper tips should produce larger curvature corrections in direct proportion to their sharpness. If the correction is absent or doesn't scale correctly, the curvature part of our model needs revision.

8.3 Distinguishing Calibration from Prediction in Main Paper Results

The hydrogen dimer results (main paper [1], Appendix C.1) constitute calibration—parameters were fitted to H_2 observables. The crystal structure predictions (Appendix C.2) constitute transfer—the same parameters were applied without refitting. The noble gas dimer results (Appendix D.1), where only tabulated van der Waals radii and the universal C_2 were used, approach genuine out-of-sample prediction.

We note that the Tier-0 validation results showing sub-percent errors for noble gas equilibrium distances are consistent with the known correlation between van der Waals radii and equilibrium separations in weakly bound systems [12], and should be interpreted as evidence of internal consistency rather than independent predictive power. True predictive tests require the protocols described in Section 8.2.

9. Relationship to Existing Theoretical Frameworks

For the general reader: Science doesn't advance in isolation. This section explains how our approach connects to methods that physicists and chemists already use, showing where it fits into the existing landscape of tools and theories.

9.1 Connection to Gordon–Kim and Density Overlap Models

The confinement picture is compatible with density-overlap models of short-range repulsion [22], which attribute the repulsive wall to kinetic energy increase when electron densities overlap. The confinement framework provides the asymptotic structure that such models approach in the near-contact limit, while density-overlap methods provide a more detailed (but computationally expensive) description at intermediate separations.

This connection deserves deeper examination. The Gordon–Kim model computes the full kinetic energy change from overlapping free-atom densities using a Thomas–Fermi or Kirzhnits-type kinetic energy functional [18, 22]. If the confinement picture is correct, the kinetic energy contribution in Gordon–Kim calculations should asymptotically approach $1/g^2$ scaling at small gap widths. This is a nontrivial prediction: the GK model does not assume confinement geometry, so agreement would constitute independent support for the confinement asymptotic from a completely different computational framework.

Published Gordon–Kim calculations for noble gas pairs (particularly He–He and Ne–Ne) extend to moderately short range [22], and more recent density-functional treatments of kinetic energy repulsion at compressed geometries may reach the near-contact regime. A systematic comparison of the kinetic energy component of GK repulsive walls — extracted in gap coordinates and analyzed for log-log slope — would provide a stringent test of the confinement picture. We note that the non-kinetic contributions in GK (electrostatic, exchange-correlation) scale more slowly and should separate cleanly from the kinetic channel at sufficiently small g. This analysis would complement Protocol 1 (Section 8.2) by testing whether the confinement asymptotic emerges from an independent and well-established computational approach, and we identify it as a high-priority near-term validation target.

For the general reader: In the 1970s, Gordon and Kim developed a model that explains atomic repulsion through the increase in kinetic energy when electron clouds overlap. Our approach is compatible with theirs — in fact, our $1/g^2$ law describes the limiting behavior that their more detailed (and more expensive) calculations should approach at very close range. Checking whether this actually happens in existing Gordon-Kim data would be powerful validation: it would show that two completely different methods of calculation arrive at the same answer. Think of it as two independent witnesses confirming the same story.

9.2 Relationship to Pseudopotential Theory

In the language of pseudopotential theory [23, 24], the confinement potential provides a physically motivated functional form for the repulsive core, replacing the empirical exponentials typically used. The systematic corrections (Section 7) correspond to the environmental dependence that pseudopotential practitioners already know is necessary but currently handle through refitting.

For the general reader: Pseudopotentials are simplified representations of atoms used in large-scale computer simulations. Currently, the repulsive part of these pseudopotentials uses exponential formulas with parameters fitted to data. Our work provides a physics-based replacement for that repulsive component, with corrections that follow naturally from the theory rather than requiring case-by-case refitting.

9.3 Complementarity with Machine-Learned Potentials

Machine-learned interatomic potentials achieve high accuracy through flexible functional forms trained on large ab initio datasets [25, 26]. The confinement asymptotic provides a physics-based constraint that could improve ML potential behavior in data-sparse regimes (extreme compression, unusual coordination environments) where training data may be limited. Incorporating $1/g^2$ as a prior or asymptotic constraint in ML architectures is a natural direction for future work.

For the general reader: Machine learning is increasingly used to build interatomic force models by training neural networks on quantum chemistry data. These models are very accurate where training data exists but can behave unpredictably in unfamiliar situations — like predicting behavior under extreme compression where few training examples exist. Our $1/g^2$ law could serve as a "safety rail" for these models: even where training data is sparse, the ML model would be constrained to produce physically correct behavior at close range. This is like teaching a self-driving car the rules of physics in addition to training it on driving footage — the physics provides a safety net in unfamiliar situations.

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10. Frequently Asked Questions

These questions anticipate common concerns about the framework and are addressed here to prevent misreadings of the scope and claims.

Q1. Are you claiming all short-range repulsion is exactly $1/g^2$? No. We claim a universal near-contact asymptotic form. Above a system-dependent crossover gap g*, additional physics (finite orbital extent, exchange, correlation) modifies this behavior, and exponential forms remain adequate representations.

Q2. Why does electronic kinetic energy appear as an interatomic potential? This is a standard consequence of the Born–Oppenheimer approximation [2, 3]. All contributions to the electronic ground-state energy—including kinetic energy—define the potential energy surface for nuclear motion. There is no new assumption here.

Q3. Pauli repulsion is smooth, not a hard wall. Why use Dirichlet boundary conditions?
Because the low-lying eigenvalues of any sufficiently steep confining potential converge asymptotically to those of a hard-wall problem (Section 4) [6, 7]. This is a standard result in semiclassical quantum mechanics, not an approximation of convenience. Boundary softness enters as a quantified correction.

Q4. Why is a one-dimensional model sufficient for a three-dimensional problem? Because the energy scale for confinement normal to the interface exceeds the transverse scale by a factor $R/g \gg 1$ near contact (Section 3) [4, 5]. This is a controlled approximation with explicit error bounds, not a dimensional reduction by fiat.

Q5. Doesn't χ_AB break the claim of universality? No. χ_AB renormalizes the amplitude of a universal functional form, exactly as Gm_1m_2 provides a system-dependent amplitude for the universal $1/r^2$ gravitational force law. Universal form with system-dependent coupling is standard physics.

Q6. How does this relate to Born–Mayer exponential potentials? Exponentials are effective finite-range representations that approximate the confinement asymptotic over typical fitting windows [8]. The confinement framework explains their success, characterizes their domain of validity, and provides principled extrapolation beyond it (Section 6).

Q7. What specific observations would falsify this model? Four concrete protocols are specified in Section 8.2: (i) ab initio log–log slopes deviating from −2 at small g, (ii) force–distance saturation below g^*, (iii) temperature dependence of C_2, and (iv) absence of predicted curvature systematics in AFM measurements.

Q8. Does this replace quantum chemistry or machine-learned potentials? No. It provides a physically grounded asymptotic constraint that complements detailed computational methods—useful for coarse-graining, parameter transfer, boundary conditions, and physics-informed ML architectures [25, 26].

Q9. What is the void-shell interpretation mentioned in the main paper? An optional physical picture that motivates the boundary conditions and organizes the correction hierarchy. The confinement derivation and all quantitative results are independent of this interpretation. See main paper [1], Appendix A.

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11. Conclusions

This companion paper establishes the theoretical foundations for the confinement-based near-contact repulsion law presented in the main paper [1]. The key results are:

1. **Born–Oppenheimer grounding**: Electronic confinement kinetic energy enters the nuclear potential energy surface through the standard BO framework [2, 3], requiring no new physical assumptions.

2. **Dimensional reduction**: One-dimensional gap confinement captures the leading three-dimensional physics because normal and transverse energy scales separate by $R/g \gg 1$ near contact [4, 5], with transverse corrections entering at quantified subleading order.
3. **Boundary condition justification**: Dirichlet conditions are asymptotic attractors of steep Pauli exclusion [6, 7], not literal hard walls, with boundary softness producing quantified corrections absorbed into gap renormalization and the $1/g$ correction tier.
4. **Participation renormalization**: Element-dependent prefactors χ_{AB} modify the amplitude of a universal functional form, bounded by physical constraints and determinable from atomic properties [12, 13]—analogous to coupling constants in other universal force laws.
5. **Crossover characterization**: The confinement asymptotic dominates below a system-dependent crossover gap g^*, with exponential forms remaining adequate above this scale. The framework provides a physical interpretation for the exponential decay length and a protocol for determining g^* empirically.
6. **Explicit falsifiability**: Four specific protocols can decisively test the framework, with the ab initio log–log slope test (Protocol 1) being immediately executable with existing computational tools [19, 20].

The framework is asymptotic in character, bounded in scope, and falsifiable by design. Its value lies not in replacing existing methods but in providing a minimal, physically transparent description of the repulsive wall that enables parameter transfer, systematic correction, and principled extrapolation into regimes where purely empirical forms lack guidance.

For the general reader — the bottom line: We've shown rigorously why atoms repel each other following a $1/g^2$ law when they get very close, building on well-established physics rather than new assumptions. We've addressed every major technical objection, connected our work to existing methods, and laid out specific experiments that would prove us wrong if the theory is incorrect. The result is a simpler, more principled tool for predicting how atoms behave under extreme conditions — with applications ranging from materials design to pharmaceutical development to understanding the behavior of matter under extreme pressures deep within planets.

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12. References

[1] K. Taylor, "Universal Near-Contact Repulsion from Quantum Confinement: A Scale-Free Effective Potential with Systematic Corrections," VERSF Theoretical Physics Program, AIDA Institute (2025).

[2] M. Born and R. Oppenheimer, "Zur Quantentheorie der Molekeln," *Annalen der Physik* **389**, 457–484 (1927).

[3] W. Kutzelnigg, "The adiabatic approximation I. The physical background of the Born–Handy ansatz," *Molecular Physics* **90**, 909–916 (1997).

[4] J. Schatzman, "On the eigenvalues of the Laplace operator on a thin set with Neumann boundary conditions," *Applicable Analysis* **61**, 293–306 (1996).

[5] L. Friedlander and M. Solomyak, "On the spectrum of the Dirichlet Laplacian in a narrow strip," *Israel Journal of Mathematics* **170**, 337–354 (2009).

[6] B. Simon, "Semiclassical analysis of low lying eigenvalues. I. Non-degenerate minima: Asymptotic expansions," *Annales de l'Institut Henri Poincaré A* **38**, 295–308 (1983).

[7] M. Reed and B. Simon, *Methods of Modern Mathematical Physics IV: Analysis of Operators* (Academic Press, New York, 1978).

[8] M. Born and J. E. Mayer, "Zur Gittertheorie der Ionenkristalle," *Zeitschrift für Physik* **75**, 1–18 (1932).

[9] E. B. Davies, "Spectral properties of thin-domain problems," in *Spectral Theory and Geometry*, London Mathematical Society Lecture Note Series **273** (Cambridge University Press, 1999).

[10] J. C. Slater, "Atomic shielding constants," *Physical Review* **36**, 57–64 (1930).

[11] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory*, 3rd ed. (Pergamon Press, Oxford, 1977).

[12] A. Bondi, "van der Waals Volumes and Radii," *Journal of Physical Chemistry* **68**, 441–451 (1964).

[13] P. Schwerdtfeger and J. K. Nagle, "2018 Table of static dipole polarizabilities of the neutral elements in the periodic table," *Molecular Physics* **117**, 1200–1225 (2019).

[14] T. C. Thompson and C. F. Bunge, "Exponential repulsive potentials from Hartree–Fock calculations," *Journal of Chemical Physics* **68**, 1281–1288 (1978).

[15] F. J. Giessibl, "Advances in atomic force microscopy," *Reviews of Modern Physics* **75**, 949–983 (2003).

[16] J. N. Israelachvili, *Intermolecular and Surface Forces*, 3rd ed. (Academic Press, Burlington, 2011).

[17] D. S. Grebenkov and B.-T. Nguyen, "Geometrical structure of Laplacian eigenfunctions," *SIAM Review* **55**, 601–667 (2013).

[18] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).

[19] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, "A fifth-order perturbation comparison of electron correlation theories," *Chemical Physics Letters* **157**, 479–483 (1989).

[20] T. H. Dunning, Jr., "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," *Journal of Chemical Physics* **90**, 1007–1023 (1989).

[21] F. J. Giessibl, S. Hembacher, H. Bielefeldt, and J. Mannhart, "Subatomic features on the silicon (111)-(7×7) surface observed by atomic force microscopy," *Science* **289**, 422–425 (2000).

[22] R. G. Gordon and Y. S. Kim, "Theory for the forces between closed-shell atoms and molecules," *Journal of Chemical Physics* **56**, 3122–3133 (1972).

[23] J. C. Phillips and L. Kleinman, "New method for calculating wave functions in crystals and molecules," *Physical Review* **116**, 287–294 (1959).

[24] D. R. Hamann, M. Schlüter, and C. Chiang, "Norm-conserving pseudopotentials," *Physical Review Letters* **43**, 1494–1497 (1979).

[25] J. Behler and M. Parrinello, "Generalized neural-network representation of high-dimensional potential-energy surfaces," *Physical Review Letters* **98**, 146401 (2007).

[26] A. P. Bartók, M. C. Payne, R. Kondor, and G. Csányi, "Gaussian approximation potentials: The accuracy of quantum mechanics, without the electrons," *Physical Review Letters* **104**, 136403 (2010).

[27] K. T. Tang and J. P. Toennies, "An improved simple model for the van der Waals potential based on universal damping functions for the dispersion coefficients," *Journal of Chemical Physics* **80**, 3726–3741 (1984).

[28] B. Cappella and G. Dietler, "Force-distance curves by atomic force microscopy," *Surface Science Reports* **34**, 1–104 (1999).

[29] S. H. Patil and K. T. Tang, "Multipolar polarizabilities and two- and three-body dispersion coefficients for alkali isoelectronic sequences," *Journal of Chemical Physics* **106**, 2298–2305 (1997).