

Bibliography for D -scaling

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Herschbach

All references by Dudley Herschbach.

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- [168] M. Dunn, T. C. Germann, D. Z. Goodson, C. A. Traynor, J. D. Morgan, D. K. Watson, and D. R. Herschbach. A LINEAR ALGEBRAIC-METHOD FOR EXACT COMPUTATION OF THE COEFFICIENTS OF THE $1/D$ EXPANSION OF THE SCHRÖDINGER-EQUATION. *J. Chem. Phys.*, 101(7):5987–6004, 1994.

Abstract: The 1/D expansion, where D is the dimensionality of space, offers a promising new approach for obtaining highly accurate solutions to the Schrodinger equation for atoms and molecules. The method typically employs an asymptotic expansion calculated to rather large order. Computation of the expansion coefficients has been feasible for very small systems, but extending the existing computational techniques to systems with more than three degrees of freedom has proved difficult. We present a new algorithm that greatly facilitates this computation. It yields exact values for expansion coefficients, with less roundoff error than the best alternative method. Our algorithm is formulated completely in terms of tensor arithmetic, which makes it easier to extend to systems with more than three degrees of freedom and to excited states, simplifies the development of computer codes, simplifies memory management, and makes it well suited for implementation on parallel computer architectures. We formulate the algorithm for the calculation of energy eigenvalues, wave functions, and expectation values for an arbitrary many-body system and give estimates of storage and computational costs.

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Abstract: Directional superpositions of the rotational states of linear molecules can be created by interaction of the polarizability with the strong electric field of an

intense laser beam. The polarizability interaction, proportional to $\cos^2(\theta)$ (with θ the angle between the molecular axis and the direction of the electric field), is a double-well potential, with end-for-end symmetry. The energy levels thus exhibit tunnel-effect splittings. We present an exact treatment, derived by transcription to an oblate spheroidal wave equation. We also develop an accurate semiclassical approximation, in which the action integral and period are evaluated using an effective potential that corresponds to one-dimensional motion. The results pertain both to rotational spectroscopy of nonpolar molecules and to alignment and trapping experiments with either nonpolar or polar molecules.

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Abstract: We examine strategies for approximating the sum of a perturbation expansion for Coulombic systems in inverse powers of the spatial dimension D using only the few lowest-order terms. Several summation methods are tested on energy expansions of the following systems: the ground state of He, the ground state of Li^+ , the first two excited S states and the lowest $3P(e)$ state of He, and the ground state of H^{2+} . The origin of the expansions, the limit $D \rightarrow \infty$, corresponds to a pseudoclassical limit, but lower-order terms are strongly affected by poles at $D = 1$, a hyperquantum limit. Two alternative methods are recommended, weighted truncation and hybrid Pade summation, which exploit these poles to reduce the summation error. In effect, these methods modify a semiclassical $1/D$ expansion by incorporating corrections that are often large. Weighted truncation appears to be slightly more dependable at very low orders, while hybrid Pade summation is preferable when more

than the three lowest-order terms are available or when the residue of the second-order pole at $D = 1$ is known. We demonstrate that the present methods are superior to the shifted-expansion method, which does not correctly model the singularity structure.

- [237] D. Z. Goodson, M. Lopezcabrera, D. R. Herschbach, and J. D. Morgan. LARGE-ORDER DIMENSIONAL PERTURBATION-THEORY FOR 2-ELECTRON ATOMS. *J. Chem. Phys.*, 97(11):8481–8496, 1992.

Abstract: An asymptotic expansion for the electronic energy of two-electron atoms is developed in powers of $\delta=1/D$, the reciprocal of the Cartesian dimensionality of space. The expansion coefficients are calculated to high order (approximately 20 to 30) by an efficient recursive procedure. Analysis of the coefficients elucidates the singularity structure in the $D \rightarrow \infty$ limit, which exhibits aspects of both an essential singularity and a square-root branch point. Pade-Borel summation incorporating results of the singularity analysis yields highly accurate energies; the quality improves substantially with increase in either D or the nuclear charge Z . For He, we obtain 9 significant figures for the ground state and 11 for the $2p^2\ 3P(e)$ doubly excited state, which is isomorphic with the ground state at $D=5$ by virtue of interdimensional degeneracy. The maximum accuracy obtainable appears to be limited only by accumulation of roundoff error in the expansion coefficients. The method invites application to systems with many electrons or subject to external fields.

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Abstract: For a nonrelativistic hydrogenic atom, the dimension dependence of the energy levels is non-singular except for a second-order pole at $D^* = 3 - 2n$, where n is the principal quantum number. For the relativistic Klein-Gordon and Dirac equations, the dimension dependence has a much more complicated singularity structure, involving branch points. For all eigenstates there are branch points at $D \pm 2Z\alpha$, where Z is the nuclear charge, α is the fine-structure constant, and $D \pm$ is independent of n but varies linearly with orbital angular momentum. For most states there is in addition a pair of branch points near D^* but slightly off the

real axis. The customary perturbation expansion in terms of Z - α gives qualitatively incorrect dimension dependence; it predicts only poles located on the real axis at D^* and $D+$, no matter how high the order of the expansion. The dimensional singularities result from the behavior at $r = 0$. The qualitatively incorrect results occur because the perturbing potential, proportional to α^2/r^2 , overwhelms the unperturbed $1/r$ potential at small r . Because of the complexity of the dimensional singularity structure, the popular "shifted expansion" method for summing the $1/D$ expansion does not work well for these equations. We demonstrate a general method for identifying the dimensional singularities that leads to an exact summation of the $1/D$ expansion for all eigenstates of both the Klein-Gordon and the Dirac equations for a particle in a Coulomb potential.

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Abstract: For a two-electron atom, many $D = 3$ states have the same energies as $D = 5$ states of lower angular momentum. Thus the energies of $3P(e)$, $1P(e)$, $3D0$, and $1D0$ states for $D = 3$ are respectively identical to those for $1S(e)$, $3S(e)$, $1P0$, and $3P0$ states at $D = 5$. We exploit these interdimensional degeneracies to obtain accurate energies for doubly excited $2pnp$ $P(e)$ states of helium at $D = 3$, with $n = 2-6$, by calculating energy eigenvalues for the singly excited $1s(n-1)s$ $S(e)$ states at $D = 5$. We also illustrate how some qualitative aspects of double-excitation spectra can be elucidated in terms of interdimensional degeneracies.

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Abstract: A nostalgic account is given of my scientific odyssey, recalling early encounters, some fateful, some just fun, with mentors, methods, and molecules. These include stories of my student years at Stanford, pursuing chemical kinetics with Harold Johnston; graduate study at Harvard, doing molecular spectroscopy with Bright Wilson; and fledgling faculty years at Berkeley, launching molecular beam studies of reaction dynamics. A few vignettes from my "ever after" era on the Harvard faculty

emphasize thematic motivations or methods inviting further exploration. An Appendix provides a concise listing of colleagues in research and the topics we have pursued.

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- [275] D. R. Herschbach. Dimensional scaling and renormalization. *Int. J. Quantum Chem.*, 57(3):295–308, 1996.

Abstract: Chief features of dimensional scaling methods are exemplified by briefly reviewing prototypical applications and recent developments. The pseudoclassical large-D limit usually can be evaluated exactly regardless of the magnitude, nature, and number of strong, nonseparable dynamical interactions. Often, this limit can be accurately linked to $D = 3$ by perturbation or interpolation methods. This is because the dimension dependence of many-body effects tends to be smooth and mild when calibrated by appropriate one- or few-body problems. A simple renormalization procedure applied to atoms with up to N similar to 100 electrons yields a major part of the correlation energy. From Hartree-Fock input, a renormalized nuclear charge is determined which renders the dimensionally scaled energy at $D \rightarrow \infty$ a good approximation to that for $D = 3$ with the actual Z . Prospects are discussed for other means to exploit dimensional scaling, including an analogous renormalization procedure for molecules. (C) 1996 John Wiley & Sons, Inc.

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Abstract: For large values of $d = 3N$, the radial distribution function of an N -particle system is sharply peaked near the hyperradius $r(m) = (d - 2)/2k_0$, where $k_0 = (2E)^{1/2}$. This fact allows an approximate separation of

the hyperradius, leading to many-dimensional hydrogen-like radial solutions. Kindred applications to dimensional scaling are also discussed, where $d = DN$, with D the spatial dimension. For the large D regime, illustrative analytic formulas are obtained giving the energy and effective nuclear charge for the lowest few S states of the helium atom.

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Abstract: We derive a simple, analytic expression for the energy splitting ΔE between the lowest pair of H_2^+ states ($1s\text{-}\sigma(g)$ and $2p\text{-}\sigma(u)$) that results from electron exchange between two protons. The calculation employs the semiclassical instanton method, with two unorthodox features which markedly simplify the treatment: (1) The double-minimum potential and corresponding wavefunctions that govern the electronic tunneling are evaluated in the large-dimension limit. (2) The time variable is rescaled to cure divergent behavior of fluctuations about the instanton path that otherwise appears because of the potential develops sharp cusps as the internuclear distance increases. By virtue of exact interdimensional degeneracies, the large- D limit yields valid results for a 3D molecule. Indeed, a simple dimensional scaling law gives ΔE for all pairs of g, u states that stem from separated atom states with $m = l = n - 1$, for $n = 1 - j$ infinity. For a wide range of internuclear distances, our analytic expression for ΔE , which pertains to the leading order in \hbar , gives for such states good agreement with comparable semiclassical methods as well as with exact numerical calculations. It is remarkable that use of the effective potential for the large-dimension limit, which is exactly calculable from classical electrostatics, yields quantitative results for electronic tunneling, an intrinsically quantal phenomenon.

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Abstract: Analytic expressions for the $D - j$ infinity limit previously evaluated for one- and two-electron diatomic molecules are compared with the familiar $D = 3$

potentials as functions of the internuclear distance R for H_2^+ , H_2 , HHe^+ , and He_2^+ . We find that the $D = 3$ potential can be obtained from the large- D limit simply by $E(3)(R) E(\infty)(R)/G(R)$, to good approximation, where the function $G(R)$ has the same form for the four molecules. Furthermore, $1 - G(R)$ has a corresponding-states property; when reduced by two parameters, it becomes the same function for all four molecules, nearly proportional to $x^2 e^{-2x}$, with x the scaled internuclear distance. This suggests that the pseudoclassical $D \rightarrow \infty$ limit may provide a useful reference for analysis of intermolecular potentials.

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Abstract: Complex energy eigenvalues which specify the location and width of quasibound or resonant states are computed to good approximation by a simple dimensional scaling method. As applied to bound states, the method involves minimizing an effective potential function in appropriately scaled coordinates to obtain exact energies in the $D \rightarrow \infty$ limit, then computing approximate results for $D = 3$ by a perturbation expansion in $1/D$ about this limit. For resonant states, the same procedure is used, with the radial coordinate now allowed to be complex. Five examples are treated: the repulsive exponential potential (e^{-r}); a squelched harmonic oscillator ($r^2 e^{-r}$); the inverted Kratzer potential (r^{-1} repulsion plus r^{-2} attraction); the Lennard-Jones potential (r^{-12} repulsion, r^{-6} attraction); and quasibound states for the rotational spectrum of the hydrogen molecule ($X^1\Sigma(g)^+$, $v = 0$, $J = 0$ to 50). Comparisons with numerical integrations and other methods show that the much simpler dimensional scaling method, carried to second-order (terms in $1/D^2$), yields good results over an extremely wide range of the ratio of level widths to spacings. Other methods have not yet evaluated the very broad H_2 rotational resonances reported here (J_l 39), which lie far above the centrifugal barrier.

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Abstract: Analytic expressions for the large-dimension limit, when renormalized by introducing a suitable effective nuclear charge ζ yield accurate $D=3$ nonrelativistic energies for ground states of many-electron atoms. Using Hartree-Fock data to estimate ζ , which typically differs from the actual charge Z by similar to 1% or less, we find this dimensional renormalization method (denoted DR-O) gives results substantially better than the HF input. Comparison of the $1/Z$ expansion for the large- D limit with that for $D=3$ atoms provides expressions for the leading error terms in the renormalized total energy and correlation energy. When configuration mixing occurs in the $Z \rightarrow \infty$ limit (as for Be and many other atoms), we find the renormalization procedure is markedly improved by including the zeroth-order mixing (denoted DR-1); this contributes a term linear in Z . Including the Z -independent term (DR-2) also improves the accuracy when zeroth-order mixing is absent (e.g., ground-state atoms with $N=2, 3,$ and $7-11$) but not otherwise. Correlation energies for atoms and cations with $N=2-18$ electrons and $Z=2-28$ are obtained with a mean error of 26% using just the large- D limit or HF input (DR-O); the mean error improves to only 5% when the leading $1/Z$ term is included (either DR-1 or DR-2). Results much better than the HF approximation are likewise obtained for the ionization potentials and electron affinities of neutral atoms.

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Abstract: We treat an analytically solvable version of the "Hooke's Law" model for a two-electron atom, in which the electron-electron repulsion is Coulombic but the electron-nucleus attraction is replaced by a harmonic oscillator potential. Exact expressions are obtained for the ground-state wave function and electron density, the Hartree-Fock solution, the correlation energy, the Kohn-Sham orbital, and, by inversion, the exchange and correlation functionals. These functionals pertain to the "intermediate" density regime ($r(s)$ greater-than-or-equal-to 1.4) for an electron gas. As a test of customary approximations employed in density functional theory, we compare our exact density, exchange, and correlation potentials and energies with results from two approximations.

These use Becke's exchange functional and either the Lee-Yang-Parr or the Perdew correlation functional. Both approximations yield rather good results for the density and the exchange and correlation energies, but both deviate markedly from the exact exchange and correlation potentials. We also compare properties of the Hooke's Law model with those of two-electron atoms, including the large dimension limit. A renormalization procedure applied to this very simple limit yields correlation energies as good as those obtained from the approximate functionals, for both the model and actual atoms.

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Abstract: Dimensional scaling generates an effective potential for the electronic structure of atoms and molecules, but this potential may acquire multiple minima for certain ranges of nuclear charges or geometries that produce symmetry breaking. Tunneling among such minima is akin to resonance among valence bond structures. Here we treat the D-dimensional H-2+ molecule ion as a prototype test case. In spheroidal coordinates it offers a separable double-minimum potential and tunneling occurs in only one coordinate; in cylindrical coordinates the potential is nonseparable and tunneling occurs in two coordinates. We determine for both cases the ground state energy splitting $\Delta E(D)$ as a function of the internuclear distance R . By virtue of exact interdimensional degeneracies, this yields the exchange energy for all pairs of g, u states of the $D = 3$ molecule that stem from separated atom states with $m = l = n - 1$, for $n = 1 - j$ infinity. We evaluate $\Delta E(D)$ by two semiclassical techniques, the asymptotic and instanton methods, and obtain good agreement with exact numerical calculations over a wide range of R . We find that for cylindrical coordinates the instanton path for the tunneling trajectory differs substantially from either a straightline or adiabatic path, but is nearly parabolic. Path integral techniques provide relatively simple means to determine the exact instanton path and contributions from fluctuations around

it. Generalizing this approach to treat multielectron tunneling in several degrees of freedom will be feasible if the fluctuation calculations can be made tractable.

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Abstract: A growing repertoire of electronic structure methods employ the spatial dimension D as an interpolation or scaling parameter. It is advantageous to transform the Schrodinger equation to remove all dependence on D from the Jacobian volume element and the Laplacian operator; this introduces a centrifugal term, quadratic in D , that augments the effective potential. Here we explicitly formulate this procedure for S states of an arbitrary many-particle system, in two variants. One version reduces the Laplacian to a quasicartesian form, and is particularly suited to evaluating the exactly solvable $D \rightarrow \infty$ limit and perturbation expansions about this limit. The other version casts the Jacobian and Laplacian into the familiar forms for $D = 3$, and is particularly suited to calculations employing conventional Rayleigh-Ritz variational methods.

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Abstract: By augmenting Hartree-Fock (HF) results for nonrelativistic ground-state energies of N -electron atoms by analytic expressions for the $D \rightarrow \infty$ limit derived by Loeser, we obtain a simple renormalization procedure which substantially enhances accuracy. A renormalized nuclear charge, $Z(\infty)$, is found which renders the dimensionally scaled energy at $D \rightarrow \infty$ a good approximation to that for $D = 3$ with the actual Z . The renormalized charge is readily evaluated by comparing the HF energy (or any other input approximation) with its $D \rightarrow \infty$ limit. For atoms with any N or Z , the computations are elementary, requiring little more than solution of a quartic equation. With only HF input in addition to the $D \rightarrow \infty$ limit, the renormalization procedure yields about 2/3 or more of the correlation energy, for neutral atoms with $N=Z = 2 \rightarrow 86$. Further improvements in the method seem feasible, but will require better means to incorporate shell-structure in the large- D limit.

- [331] S. Kais, S. M. Sung, and D. R. Herschbach. LARGE-Z AND LARGE-N DEPENDENCE OF ATOMIC ENERGIES FROM RENORMALIZATION OF THE LARGE-DIMENSION LIMIT. *Int. J. Quantum Chem.*, 49(5):657–674, 1994.

Abstract: By combining Hartree-Fock results for non-relativistic ground-state energies of N-electron atoms with analytic expressions for the large-dimension limit, we have obtained a simple renormalization procedure. For neutral atoms, this yields energies typically three-fold more accurate than the Hartree-Fock approximation. Here, we examine the dependence on Z and N of the renormalized energies $E(N, Z)$ for atoms and cations over the range $Z, N = 2 - 290$. We find that this gives for large $Z = N$ an expansion of the same form as the Thomas-Fermi statistical model, $E \sim Z^{7/3}(C_0 + C(1)Z^{-1/3} + C(2)Z^{-2/3} + C(3)Z^{-3/3} + \dots)$, with similar values of the coefficients for the three leading terms. Use of the renormalized large-D limit enables us to derive three further terms. This provides an analogous expansion for the correlation energy of the for $\Delta E \sim Z^{4/3}(\Delta C-3 + \Delta C(5)Z^{-2/3} + \Delta C(6)Z^{-3/3} + \dots)$; comparison with accurate values of ΔE available for the range Z less than or equal to 36 indicates the mean error is only about 10%. Oscillatory terms in E and ΔE are also evaluated. (C) 1994 John Wiley & Sons, Inc.

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Abstract: A Sturmian basis set is a set of solutions to the Schrodinger equation, with the potential scaled in such a way that all the members of the set correspond to the same value of the energy. We discuss, in particular, the set of Sturmian basis functions corresponding to solutions of the d-dimensional hydrogenlike wave equation. These hydrogenlike Sturmian functions are expressed in terms of Laguerre polynomials and hyperspherical harmonics. When they are used as a basis for solving the many-particle Schrodinger equation, the secular equations take on a simple form [Eq. (59)]. The necessary integrals are evaluated explicitly, and the possibility of combining the hyperspherical technique with dimensional scaling is discussed.

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Abstract: We examine the dependence on spatial dimension D of the Mayer cluster integrals that determine the virial coefficients $B(n)$ for a fluid of rigid hyperspheres. The integrals vary smoothly with D , and can be characterized analytically in both the low- D and high- D limits. Dimensional interpolation (DI) allows one to evaluate individual Mayer cluster integrals at $D = 2$ and $D = 3$ to within about 1%. The resulting low-order virial coefficients have an accuracy intermediate between those of the Percus-Yevick and hypernetted chain approximations. Much higher accuracy can be achieved by combining the DI and HNC approximations, using DI to evaluate those integrals omitted by HNC. The resulting low-order virial coefficients are more accurate than those given by any existing integral equation approximation. At higher order, the accuracy of the individual cluster integrals is insufficient to compute reliable virial coefficients from the Mayer expansion. Reasonably accurate values can still be computed, however, by taking partial sums of the Ree-Hoover reformulation of the Mayer expansion. We report hard disk virial coefficients through B_{15} and hard sphere values through B_{10} ; the maximum errors with respect to known values are about 1.2 and 4.3%, respectively. The new coefficients are in good agreement with those

obtained by expanding certain equations of state which fail to diverge until unphysical densities (those beyond closest packing), and so help to explain the surprising accuracy of some of these equations. We discuss the possibility that the exact virial expansion has a radius of convergence which corresponds to an unphysical density. Several new equations of state with desirable analytic or representational characteristics are also reported.

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Abstract: An asymptotic expansion for the electronic energy of H-2(+) is developed in inverse powers of D, the spatial dimension, and the singularity structure in the D \rightarrow ∞ limit is elucidated by analysis of the coefficients at large order (approximately 30 to 45). For the ground state and several excited states, Pade-Borel summation yields an accuracy of eight or more significant figures.

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Abstract: The molecular-orbital description of two-electron atoms [J. M. Feagin and J. S. Briggs, *Phys. Rev. A* 37, 4599 (1988)], derived from H-2+ by interchanging the roles of electrons and nuclei, is generalized to D dimensions. For H-2+ itself there exist myriad exact interdimensional degeneracies because D \rightarrow D + 2 is equivalent to m \rightarrow m + 1, augmenting by unity the projection of the electronic angular momentum on the internuclear axis. When the molecular orbitals (MO's) are transcribed to treat two-electron motion, additional constraints limit the exact degeneracies to states in D = 3 and 5, but many approximate degeneracies persist. Since the MO description emphasizes rotational properties of the two-electron atom, the link between dimension and orbital angular momentum is a pervasive feature. We use this link to classify groups of quasidegenerate doubly excited atomic energies and to explain striking similarities among certain pairs of hyperspherical or molecular-orbital two-electron potential curves.

- [577] Q. C. Shi, S. Kais, and D. R. Herschbach. Electron localization-delocalization transitions in dissociation of the C-4(-) anion: A large-D analysis. *J. Chem. Phys.*, 120(5):2199–2207, 2004.

Abstract: We present a study, employing high level ab initio methods, of electron localization-delocalization transitions along the dissociation path of the C-4(-) anion to C-2 and C-2(-). We find that at the equilibrium geometry, the symmetrical and nonsymmetrical configurations of the linear C-4(-) anion are almost isoenergetic. However, along a collinear dissociation path, the dipole moment drops abruptly to zero when the separation between the two middle carbon nuclei reaches about $R=2.15$ Angstrom. The dipole moment remains zero until about $R=2.78$ Angstrom, and then continuously increases as dissociation proceeds. This behavior is analogous to critical phenomena: The abrupt drop to zero of the dipole moment resembles a first-order phase transition, the later steady rise resembles a continuous phase transition. We show that a simple sub-Hamiltonian model, corresponding to the large-dimension limit for an electron in the field of four collinear carbon atoms, exhibits both kinds of phase transitions along the dissociation path. (C) 2004 American Institute of Physics.

- [595] S. M. Sung and D. R. Herschbach. HIDDEN SYMMETRY AND EXPLICIT SPHEROIDAL EIGENFUNCTIONS OF THE HYDROGEN-ATOM. *J. Chem. Phys.*, 95(10):7437–7448, 1991.

Abstract: The Schrodinger equation for a hydrogenic atom is separable in prolate spheroidal coordinates, as a consequence of the "hidden symmetry" stemming from the fixed spatial orientation of the classical Kepler orbits. One focus is at the nucleus and the other a distance R away along the major axis of the elliptic orbit. The separation constant- α is not an elementary function of Z or R or quantum numbers. However, for given principal quantum number n and angular momentum projection m , the allowed values of α and corresponding eigenfunctions in spheroidal coordinates are readily obtained from a secular equation of order $n - m$. We evaluate $\alpha(n,m;ZR)$ and the coefficients $g(l)$ (α) that specify the spheroidal eigenfunctions as hybrids of the familiar nlm_j hydrogen-atom states with fixed n and m but different l values. Explicit formulas and plots are given for α and $g(l)$ and for the probability distributions derived from the hybrid wave functions, $\text{SIGMA}(l)g(l)$

(α) nlm_j), for all states up through $n = 4$. In the limit $R \rightarrow \infty$ these hybrids become the solutions in parabolic coordinates, determined simply by geometrical Clebsch-Gordan coefficients that account for conservation of angular momentum and the hidden symmetry. We also briefly discuss some applications of the spheroidal eigenfunctions, particularly to exact analytic solutions of two-center molecular orbitals for special values of R and the nuclear charge ratio $Z(a)/Z(b)$.

- [598] A. Svidzinsky, G. Chen, S. Chin, M. Kim, D. X. Ma, R. Murawski, A. Sergeev, M. Scully, and D. Herschbach. Bohr model and dimensional scaling analysis of atoms and molecules. *Int. Rev. Phys. Chem.*, 27(4):665–723, 2008.

Abstract: It is generally believed that the old quantum theory, as presented by Niels Bohr in 1913, fails when applied to few electron systems, such as the H-2 molecule. Here we review recent developments of the Bohr model that connect it with dimensional scaling procedures adapted from quantum chromodynamics. This approach treats electrons as point particles whose positions are determined by optimizing an algebraic energy function derived from the large-dimension limit of the Schrodinger equation. The calculations required are simple yet yield useful accuracy for molecular potential curves and bring out appealing heuristic aspects. We first examine the ground electronic states of H-2, HeH, He-2, LiH, BeH and Li-2. Even a rudimentary Bohr model, employing interpolation between large and small internuclear distances, gives good agreement with potential curves obtained from conventional quantum mechanics. An amended Bohr version, augmented by constraints derived from Heitler-London or Hund-Mulliken results, dispenses with interpolation and gives substantial improvement for H-2 and H-3. The relation to D-scaling is emphasized. A key factor is the angular dependence of the Jacobian volume element, which competes with interelectron repulsion. Another version, incorporating principal quantum numbers in the D-scaling transformation, extends the Bohr model to excited S states of multielectron atoms. We also discuss kindred Bohr-style applications of D-scaling to the H atom subjected to superstrong magnetic fields or to atomic anions subjected to high frequency, superintense laser fields. In conclusion, we note correspondences to the prequantum bonding models of Lewis and Langmuir and to the later resonance theory of

Pauling, and discuss prospects for joining D-scaling with other methods to extend its utility and scope.

- [600] A. A. Svidzinsky, M. O. Scully, and D. R. Herschbach. Simple and surprisingly accurate approach to the chemical bond obtained from dimensional scaling. *Phys. Rev. Lett.*, 95(8):4, 2005.

Abstract: We present a new dimensional scaling transformation of the Schrodinger equation for the two electron bond. This yields, for the first time, a good description of the bond via D scaling. There also emerges, in the large-D limit, an intuitively appealing semiclassical picture, akin to a molecular model proposed by Bohr in 1913. In this limit, the electrons are confined to specific orbits in the scaled space, yet the uncertainty principle is maintained. A first-order perturbation correction, proportional to $1/D$, substantially improves the agreement with the exact ground state potential energy curve. The present treatment is very simple mathematically, yet provides a strikingly accurate description of the potential curves for the lowest singlet, triplet, and excited states of H-2. We find the modified D-scaling method also gives good results for other molecules. It can be combined advantageously with Hartree-Fock and other conventional methods.

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Abstract: It is generally believed that the old quantum theory, as presented by Niels Bohr in 1913, fails when applied to few electron systems, such as the H-2 molecule. Here, we find previously undescribed solutions within the Bohr theory that describe the potential energy curve for the lowest singlet and triplet states of H-2 about as well as the early wave mechanical treatment of Heitler and London. We also develop an interpolation scheme that substantially improves the agreement with the exact ground-state potential curve of H-2 and provides a good description of more complicated molecules such as LiH, Li-2, BeH, and He-2.

- [647] Q. Wei, S. Kais, and D. Herschbach. Dimensional scaling treatment of stability of atomic anions induced by superintense, high-frequency laser fields. *J. Chem. Phys.*, 127(9):6, 2007.

Abstract: We show that dimensional scaling, combined with the high-frequency Floquet theory, provides useful means to evaluate the stability of gas phase atomic anions in a superintense laser field. At the large-dimension limit ($D \rightarrow \infty$), in a suitably scaled space, electrons become localized along the polarization direction of the laser field. We find that calculations at large D are much simpler than $D=3$, yet yield similar results for the field strengths needed to bind an "extra" one or two electrons to H and He atoms. For both linearly and circularly polarized laser fields, the amplitude of quiver motion of the electrons correlates with the detachment energy. Despite large differences in scale, this correlation is qualitatively like that found between internuclear distances and dissociation energies of chemical bonds. (C) 2007 American Institute of Physics.

- [648] Q. Wei, S. Kais, and D. Herschbach. Dimensional scaling treatment of stability of simple diatomic molecules induced by superintense, high-frequency laser fields. *J. Chem. Phys.*, 129(21):8, 2008.

Abstract: We present results obtained using dimensional scaling with high-frequency Floquet theory to evaluate the stability of gas phase simple diatomic molecules in superintense laser fields. The large- D limit provides a simple model that captures the main physics of the problem, which imposes electron localization along the polarization direction of the laser field. This localization markedly reduces the ionization probability and can enhance chemical bonding when the laser strength becomes sufficiently strong. We find that energy and structure calculations at the large-dimensional limit ($D \rightarrow \infty$) for stabilities of H_2^+ , H_2^- , and He_2^- in superintense laser fields are much simpler than at $D=3$, yet yield similar results to those found from demanding ab initio calculations. We also use the large- D model to predict the stability of H_2^- and the field strength needed to bind the "extra" electron to the H_2 molecule.