

Bibliography for D -scaling

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Goodson

All references by David Goodson.

References

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Abstract: First-order dimensional perturbation theory is used to construct a Hamiltonian for the H-2(+) molecule without the Born-Oppenheimer approximation. The physical model that emerges has the three particles undergoing harmonic oscillations about a bent symmetric configuration. Despite its simplicity, the theory yields correct results for the ground-state energy, for the equilibrium internuclear distance, and for vibrational frequencies. Although the standard dimensional continuation of the Schrodinger equation leads to dissociation at large D , this model remains stable due to a quadratic polynomial in $1/D$ that is included in the potential energy. This Hamiltonian is a suitable starting point for a large-order perturbation expansion in $1/D$. (C) 1996 John Wiley & Sons, Inc.

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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: The convergence of large-order expansions in $\delta = 1/D$, where D is the dimensionality of coordinate space, for energies $E(\delta)$ of Coulomb systems is strongly affected by singularities at $\delta = 1$ and Pade'-Borel approximants with modifications that completely remove the singularities at $\delta = 1$ and remove the dominant singularity at $\delta = 0$ are demonstrated. A renormalization of the interelectron repulsion is found to move the dominant singularity of the Borel function $F(\delta) = \sum_j E_j / j!$, where E_j are the expansion coefficients of the energy with singularity structure removed at $\delta = 1$, farther from the origin and thereby accelerate summation convergence. The ground-state energies of He and H-2(+) are used as test cases. The new methods give significant improvement over previous summation methods. Shifted Borel summation using $F_m(\delta) = \sum_j E_j / \Gamma(j + m)$ is considered. The standard deviation of results calculated with different values of the shift parameter m is

proposed as a measure of summation accuracy. (C) 1998 American Institute of Physics. [S0022-2488(98)04210-8].

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Abstract: A method is developed for using large-order perturbation theory to solve the systems of coupled differential equations that result from the variational solution of the Schrodinger equation with wave functions of product form. This is a noniterative, computationally efficient way to solve self-consistent-field (SCF) equations. Possible applications include electronic structure calculations using products of functions of collective coordinates that include electron correlation, vibrational SCF calculations for coupled anharmonic oscillators with selective coupling of normal modes, and ab initio calculations of molecular vibration spectra without the Born-Oppenheimer approximation.

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Abstract: Rational and algebraic Pade approximants are applied to Moller-Plesset (MP) perturbation expansions of energies for a representative sample of atoms and small molecules. These approximants can converge to the full configuration-interaction result even when partial summation diverges. At order MP2 (the first order beyond the Hartree-Fock approximation), the best results are obtained from the rational $[0/1]$ Pade approximant of the total energy. At MP3 rational and quadratic approximants are about equally good, and better than partial summation. At MP4, MP5, and MP6, quadratic approximants appear to be the most dependable method. The success of the quadratic approximants is attributed to their ability to model the singularity structure in the complex plane of the perturbation parameter. Two classes of systems are distinguished according to whether the dominant singularity is in the positive half plane (class A) or the negative half plane (class B). A new kind of quadratic approximant, with a constraint on one of its constituent polynomials, gives better results than conventional approximants for class B systems at MP4, MP5, and MP6. For CH₃ with the C-H distance at twice the equilibrium value the quadratic approximants yield a complex value for the ground-state electronic energy.

This is interpreted as a resonance eigenvalue embedded in the ionization continuum. (C) 2000 American Institute of Physics. [S0021-9606(00)30208-2].

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Abstract: The accuracy of Moller-Plesset (MP) perturbation theory and coupled-cluster (CC) theory can be significantly improved, at essentially no increase in computational cost, by using summation approximants that model the way in which these theories converge to the full configuration interaction limit. Approximants for MP4 and CCSD(T) are presented, their size scaling is analyzed, and the functional analysis of the MP energy, on which the MP4 approximant is based, is discussed. The MP approximants are shown to have a form that is appropriate for describing resonance energies. (C) 2003 Wiley Periodicals, Inc.

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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 Padé 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.

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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 nonsingular 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 $D \pm \sqrt{2Z\alpha}$, where Z is

the nuclear charge, α is the fine-structure constant, and $D+$ 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 $Z\alpha$ 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: The usefulness of Moller-Plesset perturbation theory, a standard technique of quantum chemistry, is determined by singularities in the corresponding energy function in the complex plane of the perturbation parameter. A method is developed that locates singularities from fourth-order perturbation series, using quadratic approximants with bilinear conformal mappings. (c) 2006 Elsevier B.V. All rights reserved.

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Abstract: Large-order dimensional perturbation theory, which yields high accuracy for ground-state energies, is applied here to excited states of the two-electron atom. Expansion coefficients are computed recursively using the moment method, which we formulate in terms of normal coordinates. We consider the first two excited S states of helium, corresponding, at the large-dimension limit, to one quantum in either the antisymmetric-stretch normal mode or the symmetric-stretch normal mode. Comparison with the hydrogenic limit has identified these states as $1s\ 2s\ 3S$ and $1s2s\ 1S$, respectively. We sum the $1/D$ expansions at $D = 3$, using summation procedures that take into account the dimensional singularity structure of the eigenvalues, and find convergence at $D = 3$ to the eigenvalues predicted by the hydrogenic assignments, despite apparent qualitative differences between the eigenfunctions at large D and those at $D = 3$. In the $D \rightarrow \infty$ limit, the electrons are equidistant from the nucleus. Our results for $1s2s$ energies appear to imply that the shell structure is properly accounted for by terms in the expansion beyond the lowest order. This robustness of the $1/D$ expansion suggests that the method will be applicable to many-electron systems.

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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 renormalization of the D-dimensional Hamiltonian is developed to ensure that the large-D limit corresponds to a single well at any value of the internuclear distance R. This avoids convergence problems caused by a symmetry-breaking transition that is otherwise expected to occur when R is approximately equal to the equilibrium bond distance R-eq, With larger R giving a double well. This symmetry breaking has restricted the applicability of large-order perturbation theory in 1/D to cases where R is significantly less than R-eq. The renormalization greatly extends the range of R for which the large-order expansion can be summed. A numerical demonstration is presented for H-2(+). The 1/D expansions are summed using Pade-Borel approximants with modifications that explicitly model known singularity structure.

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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: 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: 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 $D \rightarrow \infty$ 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: Perturbation theory is used to perform non-iterative calculations of energy eigenvalues of the coupled ordinary differential equations that result from imposing separability assumptions in terms of normal coordinates on vibrational wavefunctions. Various model Hamiltonians with 2 or 3 coupled normal modes are studied and the increase of computational cost with the number of degrees of freedom is analysed. Quadratic Pade approximants of the perturbation expansions are rapidly convergent, and directly yield complex numbers for resonance eigenvalues. For a 3-mode system, results are obtained within partial separability assumptions, with a pair of modes left coupled. Large-order perturbation theory with partial separability is suggested as an alternative to low-order exact perturbation theory.

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Abstract: A recently developed perturbation theory for solving self-consistent field equations is applied to the hydrogen atom in a strong magnetic field. This system

has been extensively studied using other methods and is therefore a good test case for the new method. The perturbation theory yields summable large-order expansions. The accuracy of the self-consistent field approximation varies according to field strength and quantum state but is often higher than the accuracy from adiabatic approximations. A new derivation is presented for the asymptotic adiabatic approximation, the most useful of the adiabatic approaches. This derivation uses semiclassical perturbation theory without invoking an adiabatic hypothesis. (C) 1998 John Wiley & Sons, Inc. Int J Quant Chem 69: 183-192, 1998.

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Abstract: The divergent Rayleigh-Schrodinger perturbation expansions for energy eigenvalues of cubic, quartic, sextic and octic oscillators are summed using algebraic approximants. These approximants are generalized Pade approximants that are obtained from an algebraic equation of arbitrary degree. Numerical results indicate that given enough terms in the asymptotic expansion the rate of convergence of the diagonal staircase approximant sequence increases with the degree. Different branches of the approximants converge to different branches of the function. The success of the high-degree approximants is attributed to their ability to model the function on multiple sheets of the Riemann surface and to reproduce the correct singularity structure in the limit of large perturbation parameter. An efficient recursive algorithm for computing the diagonal approximant sequence is presented.

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Abstract: The convergence behavior of Moller-Plesset (MP) perturbation series is governed by the singularity structure of the energy, with the energy treated as a function of the perturbation parameter. Singularity locations, determined from quadratic approximant analysis of high-order series, are presented for a variety of atoms and small molecules. These results can be used as benchmarks for understanding the convergence of low-order methods such as MP4 and for developing and

testing summation methods that model the singularity structure. The positions and types of singularities confirm previous qualitative predictions based on functional analysis of the Schrodinger equation. (c) 2006 American Institute of Physics.

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Abstract: It has been suggested [F. H. Stillinger, *J. Chem. Phys.* 112, 9711 (2000)] that the convergence or divergence of Moller-Plesset perturbation theory is determined by a critical point at a negative value of the perturbation parameter z at which an electron cluster dissociates from the nuclei. This conjecture is examined using configuration-interaction computations as a function of z and using a quadratic approximant analysis of the high-order perturbation series. Results are presented for the He, Ne, and Ar atoms and the hydrogen fluoride molecule. The original theoretical analysis used the true Hamiltonian without the approximation of a finite basis set. In practice, the singularity structure depends strongly on the choice of basis set. Standard basis sets cannot model dissociation to an electron cluster, but if the basis includes diffuse functions then it can model another critical point corresponding to complete dissociation of all the valence electrons. This point is farther from the origin of the z plane than is the critical point for the electron cluster, but it is still close enough to cause divergence of the perturbation series. For the hydrogen fluoride molecule a critical point is present even without diffuse functions. The basis functions centered on the H atom are far enough from the F atom to model the escape of electrons away from the fluorine end of the molecule. For the Ar atom a critical point for a one-electron ionization, which was not previously predicted, seems to be present at a positive value of the perturbation parameter. Implications of the existence of critical points for quantum-chemical applications are discussed. (C) 2005 American Institute of Physics.

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Abstract: A very efficient large-order perturbation theory is formulated for the nuclear motion of a linear tri-

atomic molecule. All coupling between vibration and rotation is included. To demonstrate the method, all of the experimentally observed rotational energies, with values of J almost up to 100, for the ground and first excited vibrational states of CO_2 and for the ground vibrational states of N_2O and of OCS are calculated. The perturbation expansions reported here are rapidly convergent. The perturbation parameter is $D^{-1/2}$, where D is the dimensionality of space. Increasing D is qualitatively similar to increasing the angular momentum quantum number J . Therefore, this approach is especially suited for states with high rotational excitation. The computational cost of the method scales only in proportion to $JN(\nu)^{5/3}$, where $N(\nu)$ is the size of the vibrational basis set. (C) 1997 American Institute of Physics.

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Abstract: The standard dimensional continuation of the Schrodinger equation, in which the kinetic energy is generalized to arbitrary D , while the potential energy is left unchanged, leads to dissociation of H_2+ in the limit of large D if the nuclei are allowed to move freely. In general, the definition chosen for the D -dimensional Schrodinger equation is arbitrary as long as the correct equation results at $D = 3$. We propose a mild dimension dependence for the potential of the internuclear repulsion. This yields a stable and physically reasonable chemical bond in the limit $D \rightarrow \infty$ and can therefore be used as the starting point for a dimensional perturbation theory without the Born-Oppenheimer approximation.

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