

# Bibliography for $D$ -scaling

May 8, 2009

## Kais

All references by Sabre Kais.

## References

- [200] A. Ferron, P. Serra, and S. Kais. Dimensional scaling for stability of two particles in a dipole field. *Chem. Phys. Lett.*, 461(1-3):127–130, 2008.

**Abstract:** We present dimensional scaling calculations for the critical parameters needed to bind one and two-electrons to a finite linear dipole field and the stability diagram for the hydrogen-antihydrogen like molecules. We find that calculations at the large-D limit are much simpler than  $D = 3$ , yet yield similar results for the critical parameters and the stability diagrams. (C) 2008 Elsevier B. V. All rights reserved.

- [201] A. Ferron, P. Serra, and S. Kais. Critical conditions for stable dipole-bound dianions. *J. Chem. Phys.*, 128(4):6, 2008.

**Abstract:** We present finite size scaling calculations of the critical parameters for binding two electrons to a finite linear dipole field. This approach gives very accurate results for the critical parameters by using a systematic expansion in a finite basis set. A complete ground state stability diagram for the dipole-bound dianion is obtained using accurate variational and finite size scaling calculations. We also study the near threshold behavior of the ground state energy by calculating its critical exponent.

- [202] A. Ferron, P. Serra, and S. Kais. Stability conditions for hydrogen-antihydrogen-like quasimolecules. *Phys. Rev. A*, 77(5):5, 2008.

**Abstract:** We present a detailed study of the stability conditions of hydrogen-antihydrogen-like quasimolecules using both variational and finite-size scaling calculations. The stability diagram of the nuclear charge  $Z$  as a function of the internuclear distance  $R$  shows bound and unbound regions separated by a first-order critical line. Calculations of the leptonic annihilation rate show a peculiar behavior for nuclear charges  $Z \geq 2$ , which was not observed for the hydrogen-antihydrogen quasimolecule; it goes through a maximum before it decays exponentially for large interhadronic distances. This might have a practical impact on the study of stability of matter-antimatter systems.

- [220] T. C. Germann and S. Kais. LARGE-ORDER DIMENSIONAL PERTURBATION-THEORY FOR COMPLEX ENERGY EIGENVALUES. *J. Chem. Phys.*, 99(10):7739–7747, 1993.

**Abstract:** Dimensional perturbation theory is applied to the calculation of complex energies for quasibound, or resonant, eigenstates of central potentials. Energy coefficients for an asymptotic expansion in powers of  $1/\kappa$ , where  $\kappa = D + 2l$  and  $D$  is the Cartesian dimensionality of space, are computed using an iterative matrix based procedure. For effective potentials which contain a minimum along the real axis in the  $\kappa \rightarrow \infty$  limit, Hermite-Pade summation is employed to obtain complex eigenenergies from real expansion coefficients. For repulsive potentials, we simply allow the radial coordinate to become complex and obtain complex expansion coefficients. Results for ground and excited states are presented for squelched harmonic oscillator ( $V(r) = V_0 r^2 e^{-r}$ ) and Lennard-Jones (12-6) potentials. Bound and quasibound rovibrational states for the hydrogen molecule are calculated from an analytic potential. We also describe the calculation of resonances for the hydrogen atom Stark effect by using the separated equations in parabolic coordinates. The methods used here should be readily extendable to systems with multiple degrees of freedom.

- [221] T. C. Germann and S. Kais. Dimensional perturbation theory for Regge poles. *J. Chem. Phys.*, 106(2):599–604, 1997.

**Abstract:** We apply dimensional perturbation theory to the calculation of Regge pole positions, providing a systematic improvement to earlier analytic first-order results. We consider the orbital angular momentum  $l$  as a function of spatial dimension  $D$  for a given energy  $E$ , and expand

l in inverse powers of  $\kappa=(D-1)/2$ . It is demonstrated for both bound and resonance states that the resulting perturbation series often converges quite rapidly, so that accurate quantum results can be obtained via simple analytic expressions given here through third order. For the quartic oscillator potential, the rapid convergence of the present  $l(D;E)$  series is in marked contrast with the divergence of the more traditional  $E(D;l)$  dimensional perturbation series, thus offering an attractive alternative for bound state problems. (C) 1997 American Institute of Physics.

- [319] S. Kais and G. Beltrame. DIMENSIONAL SCALING FOR REGGE TRAJECTORIES. *J. Phys. Chem.*, 97(10):2453–2456, 1993.

**Abstract:** Using dimensional scaling, we were able to obtain a systematic expansion for Regge trajectories in  $1/\kappa$ , where  $\kappa = (D-1)/2$  and  $D$  is the number of spatial dimensions. Bound states for the power-law potential were obtained from Regge trajectories by requiring the angular momentum quantum number to take on positive integer values. For scattering states, we calculated the positions of Regge poles for the Lennard-Jones(6,4) and (12,6)potentials. The results to first order in  $1/\kappa$  were in good agreement with both semiclassical and quantum calculations. The same expansion was used to obtain the positions of Regge poles for complex optical potentials. The results for the Lennard-Jones (I 2,6) potential perturbed by an imaginary term were in excellent agreement with the semiclassical calculations.

- [320] S. Kais and R. Bleil. CHARGE RENORMALIZATION AT THE LARGE-D LIMIT FOR N-ELECTRON ATOMS AND WEAKLY-BOUND SYSTEMS. *J. Chem. Phys.*, 102(19):7472–7478, 1995.

- [321] S. Kais, D. D. Frantz, and D. R. Herschbach. ELECTRONIC TUNNELING IN H-2+ EVALUATED FROM THE LARGE-DIMENSION LIMIT. *Chem. Phys.*, 161(3):393–402, 1992.

**Abstract:** We derive a simple, analytic expression for the energy splitting  $\Delta E$  between the lowest pair of H<sub>2</sub><sup>+</sup> states (1s- $\sigma(g)$  and 2p- $\sigma(u)$ ) 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 DELTA-E for all pairs of g, u states that stem from separated atom states with  $m = l = n - 1$ , for  $n = 1 - i$  infinity. For a wide range of internuclear distances, our analytic expression for DELTA-E, 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.

- [322] S. Kais, T. C. Germann, and D. R. Herschbach. LARGE-DIMENSION LIMIT YIELDS GENERIC REDUCED POTENTIAL CURVES FOR H<sub>2</sub><sup>+</sup>, H<sub>2</sub>, HHe<sup>+</sup>, AND He-2(2<sup>+</sup>). *J. Phys. Chem.*, 98(43):11015–11017, 1994.

**Abstract:** Analytic expressions for the  $D \rightarrow \infty$  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<sub>2</sub><sup>+</sup>, H<sub>2</sub>, HHe<sup>+</sup>, and He-2(2<sup>+</sup>). We find that the  $D = 3$  potential can be obtained from the large-D limit simply by  $E(3)(R) \approx E(\infty)(R)/G(R)$ , 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.

- [323] S. Kais and D. R. Herschbach. DIMENSIONAL SCALING FOR QUASI-STATIONARY STATES. *J. Chem. Phys.*, 98(5):3990–3998, 1993.

**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 ( $J \approx 39$ ), which lie far above the centrifugal barrier.

- [324] S. Kais and D. R. Herschbach. THE  $1/Z$  EXPANSION AND RENORMALIZATION OF THE LARGE-DIMENSION LIMIT FOR MANY-ELECTRON ATOMS. *J. Chem. Phys.*, 100(6):4367–4376, 1994.

**Abstract:** Analytic expressions for the large-dimension limit, when renormalized by introducing a suitable effective nuclear charge  $z$  yield accurate  $D=3$  nonrelativistic energies for ground states of many-electron atoms. Using Hartree-Fock data to estimate  $z$ , 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  $N=2-18$  elec-

trons 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.

- [325] S. Kais, D. R. Herschbach, N. C. Handy, C. W. Murray, and G. J. Laming. DENSITY FUNCTIONALS AND DIMENSIONAL RENORMALIZATION FOR AN EXACTLY SOLVABLE MODEL. *J. Chem. Phys.*, 99(1):417–425, 1993.

**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.

- [326] S. Kais, D. R. Herschbach, and R. D. Levine. DIMENSIONAL SCALING AS A SYMMETRY OPERATION. *J. Chem. Phys.*, 91(12):7791–7796, 1989.
- [327] S. Kais, J. D. Morgan, and D. R. Herschbach. ELECTRONIC TUNNELING AND EXCHANGE ENERGY IN THE D-DIMENSIONAL HYDROGEN-MOLECULE ION. *J. Chem. Phys.*, 95(12):9028–9041, 1991.

**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 non-separable 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.

- [328] S. Kais, J. P. Neirotti, and P. Serra. Phase transitions and the stability of atomic and molecular ions. *Int. J. Mass Spectrom.*, 182:23–29, 1999.

**Abstract:** Quantum phase transitions at absolute zero temperature can take place as some parameter in the Hamiltonian of the system is varied. For such transitions, crossing the phase boundary means that the quantum ground state changes in some fundamental way. For the Hamiltonian of N-electron atoms, this parameter is taken to be the nuclear charge. As the nuclear charge reaches a critical point, the quantum ground state changes its characters from being bound to being degenerate or absorbed by a continuum. We describe here a method to calculate the critical nuclear charge for which an atom can bind an extra electron to form a stable negative ion. The estimate of the critical nuclear charge will be used to explain and

predict the stability of atomic negative ions. The method can be generalized to predict the stability of molecular negative ions. A detailed calculation for the critical parameters for two center molecular ions is also included. (C) 1999 Elsevier Science B.V.

- [329] S. Kais and P. Serra. Quantum critical phenomena and stability of atomic and molecular ions. *Int. Rev. Phys. Chem.*, 19(1):97–121, 2000.

**Abstract:** In this review we discuss quantum phase transitions and the mapping between symmetry breaking of electronic structure configurations at the large-dimension limit and mean-field theory of phase transitions. We show that the finite size scaling method can be used for the calculations of the critical parameters of the few-body Schrodinger equation. In this approach, the finite size corresponds to the number of elements in a complete basis set used to expand the exact eigenfunction of a given Hamiltonian. The critical parameters such as the critical nuclear charges will be used to explain and predict the stability of atomic and molecular negative ions. For N-electron atoms with  $2 \leq N \leq 86$ , results show that, at most, only one electron can be added to a free atom in the gas phase. However, doubly charged atomic negative ions might exist in a strong magnetic field.

- [330] S. Kais, S. M. Sung, and D. R. Herschbach. ATOMIC ENERGIES FROM RENORMALIZATION OF THE LARGE-DIMENSION LIMIT. *J. Chem. Phys.*, 99(7):5184–5196, 1993.

**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  $N=Z \leq 86$ . 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 threefold 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,  $N = 2 - i$  290. We find that this gives for large  $Z = N$  an expansion of the same form as the Thomas-Fermi statistical model,  $E - i Z(7/3)(C_0 + C(1)Z(-1/3) + C(2)Z(-2/3) + C(3)Z(-3/3) + \dots)$ , 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  $\Delta E - i Z(4/3)(\Delta C_3 + \Delta C(5)Z(-2/3) + \Delta C(6)Z(-3/3) + \dots)$ ; comparison with accurate values of  $\Delta E$  available for the range Z less than or equal to 36 indicates the mean error is only about 10%. Oscillatory terms in E and  $\Delta E$  are also evaluated. (C) 1994 John Wiley & Sons, Inc.

- [374] J. G. Loeser, Z. Zhen, S. Kais, and D. R. Herschbach. DIMENSIONAL INTERPOLATION OF HARD-SPHERE VIRIAL-COEFFICIENTS. *J. Chem. Phys.*, 95(6):4525–4544, 1991.

**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.

- [447] J. P. Neirotti, P. Serra, and S. Kais. Critical parameters for the heliumlike atoms: A phenomenological renormalization study. *J. Chem. Phys.*, 108(7):2765–2770, 1998.

**Abstract:** A mapping between the quantum few-body problem and its classical mechanics pseudo-system analog is used to study the critical parameters for the helium isoelectronic sequence. The critical point is the critical value of the nuclear charge  $Z(c)$ , for which the energy of a bound state becomes degenerate with a threshold. A finite-size scaling ansatz in the form of a phenomenological renormalization equation is used to obtain very accurate results for the critical point of the ground-state energy,  $\lambda(c) = 1/Z(c) = 1.0976 \pm 0.0004$ , as well as for the excited  $2p(2) P-3$  state,  $\lambda(c) = 1.0058 \pm 0.0017$ . The results for the critical exponents  $\alpha$  and  $\nu$  are also included. (C) 1998 American Institute of Physics.

- [564] A. V. Sergeev and S. Kais. Variational principle for critical parameters of quantum systems. *J. Phys. A-Math. Gen.*, 32(39):6891–6896, 1999.

**Abstract:** The variational principle for eigenvalue problems with a nonidentity weight operator is used to establish upper or lower bounds on critical parameters of quantum systems. Three problems from atomic physics are considered as examples. Critical screening parameters for

the exponentially screened Coulomb potential are found using a trial function with one nonlinear variational parameter. The critical charge for the helium isoelectronic series is found using a Hylleraas-type trial function. Finally, critical charges for the same system subjected to a magnetic field are found using a product of two hydrogen-like basis sets.

- [565] P. Serra and S. Kais. Critical phenomena for electronic structure at the large-dimension limit. *Phys. Rev. Lett.*, 77(3):466–469, 1996.

**Abstract:** We show that the symmetry breaking of the electronic structure configurations at the large-D limit is completely analogous to the standard phase transitions and critical phenomena in statistical mechanics. Electronic structure at the large-D limit exhibits critical points with mean field critical exponents ( $\beta = 1/2$ ,  $\alpha = 0(\text{dis})$ ,  $\delta = 3$ , and  $\gamma = 1$ ). The complete mapping is presented for the Hartree-Fock two-electron atom in weak electric field and the two Coulomb center problems.

- [566] P. Serra and S. Kais. Multicritical phenomena for the hydrogen molecule at the large-dimension limit. *Chem. Phys. Lett.*, 260(1-2):302–308, 1996.

**Abstract:** We show that symmetry breaking of the electronic structure configurations for the Hartree-Fock hydrogen molecule at the large-dimension limit can be described as standard phase transitions. The phase diagram in the internuclear distance-nuclear charge plane shows three different stable phases corresponding to different electronic structure configurations. This phase diagram is characterized by a bicritical point where the two continuous phase transition lines join a first order transition line.

- [567] P. Serra and S. Kais. Mean field phase diagrams for one-electron molecules. *J. Phys. A-Math. Gen.*, 30(5):1483–1493, 1997.

**Abstract:** We describe a simple model for symmetry breaking of electronic structure configurations of one-electron systems. This model involves generalizing the problem to D-dimensional space and finding the solution at  $D \rightarrow \infty$ , a semiclassical limit which can be solved exactly. The large-D limit model reduces the problem to a variational calculation which is equivalent to mean-field theories of critical phenomena in statistical mechanics. We

show that symmetry breaking of electronic structure configurations can be described as standard phase transitions. Rich phase diagrams with multicritical points are reported for both linear and planar one-electron systems.

- [568] P. Serra and S. Kais. Phase transitions for N-electron atoms at the large-dimension limit. *Phys. Rev. A*, 55(1):238–247, 1997.

**Abstract:** Symmetry breaking of electronic structure configurations for N-electron atoms in weak magnetic and electric fields at the large-dimension limit is described in terms of standard phase transitions. This symmetry breaking, which leads to ionization, is completely analogous to phase transitions and critical phenomena in statistical mechanics. This analogy is shown by allowing the nuclear charge to play a role analogous to temperature in statistical mechanics. For the exact solution of N-electron atoms at the large-dimension limit, the symmetry breaking is shown to be a first-order phase transition. For the special case of two-electron atoms, the first-order transition shows a triple point where three phases with different symmetry coexist. Treatment of the Hartree-Fock solution reveals a different kind of symmetry breaking where second-order phase transitions exist for N=2. We show that Hartree-Fock two-electron atoms in a weak external electric field exhibit a critical point with mean field critical exponents ( $\beta = 1/2$ ,  $\alpha = 0$ (dis),  $\delta = 3$ , and  $\gamma = 1$ ).

- [569] P. Serra, S. Kais, and J. P. Neirotti. Finite-size scaling method for the stability of atomic and molecular ions. *Physica A*, 283(1-2):65–73, 2000.

**Abstract:** Phase transitions at absolute: zero temperature can take place as some parameter in the Hamiltonian of the system is varied. For the Hamiltonian of N-electron atoms, this parameter is taken to be the nuclear charge. As the nuclear charge reaches a critical point, the quantum ground state changes its characters from being bound to being degenerate or absorbed by a continuum. We describe the large-dimension approximation and the finite-size scaling method to calculate the critical nuclear charge for which an atom can bind an extra electron to form a stable negative ion. Results show that, as most, only one electron can be added to a free atom in the gas phase. The existence of doubly charged atomic negative ions in a strong magnetic field will be discussed. (C) 2000 Elsevier Science B.V. All rights reserved.

- [575] Q. C. Shi and S. Kais. Finite size scaling for critical parameters of simple diatomic molecules. *Mol. Phys.*, 98(19):1485–1493, 2000.

**Abstract:** We use the finite size scaling method to study the critical points, points of non-analyticity, of the ground state energy as a function of the coupling parameters in the Hamiltonian. In this approach, the finite size corresponds to the number of elements in a complete basis set used to expand the exact eigenfunction of a given molecular Hamiltonian. To illustrate this approach, we give detailed calculations for systems of one electron and two nuclear centres,  $Z(+)\text{e}(+)Z(+)$ . Within the Born-Oppenheimer approximation, there is no critical point, but without the approximation the system exhibits a critical point at  $Z = Z(c) = 1.228\ 279$  when the nuclear charge,  $Z$ , varies. We show also that the dissociation occurs in a first-order phase transition and calculate the various related critical exponents. The possibility of generalizing this approach to larger molecular systems using Gaussian basis sets is discussed.

- [576] Q. C. Shi and S. Kais. Quantum criticality at the large-dimensional limit: Three-body coulomb systems. *Int. J. Quantum Chem.*, 85(4-5):307–314, 2001.

**Abstract:** We present quantum phase transitions and critical phenomena at the large-dimension ( $D$ ) limit for three-body ABA Coulomb systems with charges ( $Q, q, Q$ ) and masses ( $M, m, M$ ). The Hamiltonian depends linearly on two parameters  $\lambda = Q/q$  and  $k = [1 + (m/M)](-1)$ . The system exhibits critical points with mean field critical exponents ( $\alpha = 0, \beta = 1/2, \delta = 3, \gamma = 1$ ). We calculate the critical curve  $\lambda(c)$  ( $\kappa$ ) through which all systems undergo a continuous-phase transition from the symmetrical configuration, the two like particles have the same distance from the reference particle, to the unsymmetrical phase. The critical curve at  $D \rightarrow \infty$  limit is a convex function of  $\kappa$  and very similar to the one obtained at  $D = 3$  with variational calculations. We also calculated the line of zero angular correlation in the mass polarization term, which separates the symmetrical phase to an atom-like region and a molecule-like region. (C) 2001 John Wiley & Sons, Inc.

- [577] Q. C. Shi, S. Kais, and D. R. Herschbach. Electron localization-delocalization transitions in dissociation of the  $\text{C}^{-4}$  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.

- [578] Q. C. Shi, S. Kais, F. Remacle, and R. D. Levine. On the crossing of electronic energy levels of diatomic molecules at the large-D limit. *J. Chem. Phys.*, 114(22):9697–9705, 2001.

**Abstract:** Analytical and numerical results are presented for the intersection of electronic energies of the same space symmetry for electrons in the field of two Coulomb centers in D-dimensions. We discuss why such crossings are allowed and may be less "exceptional" than one could think because even for a diatomic molecule there is more than one parameter in the electronic Hamiltonian. For a one electron diatomic molecule at the large-D limit, the electronic energies are shown analytically to diverge quadratically from the point of their intersection. The one electron two Coulomb centers problem allows a separation of variables even when the charges on the two centers are not equal. The case of two electrons, where their Coulombic repulsion precludes an exact symmetry, is therefore treated in the large-D limit. It is then found that, in addition to the quadratic intersection, there is also a curve crossing where the energies diverge linearly. (C) 2001 American Institute of Physics.

- [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.

- [75] R. Bleil, A. Faliks, M. Miletic, and S. Kais. CHARGE RENORMALIZATION AT THE LARGE- $D$  LIMIT FOR DIATOMIC MOLECULES. *J. Chem. Phys.*, 103(15):6529–6535, 1995.

**Abstract:** The charge renormalization procedure for the calculation of the correlation energy of atoms utilizing the analytically known large- $D$  limit solutions for the exact and Hartree-Fock equations is extended to diatomic

molecules. This procedure is based on the variation of the nuclear charge,  $Z$ , and internuclear distance,  $R$ , of the Hartree-Fock Hamiltonian such that the Hartree-Fock energy will be significantly closer to the exact energy. We calculate to first order in  $\delta Z$  the leading contribution to the correlation energy by changing the nuclear charge to some renormalized nuclear charge,  $Z(i)(R) - \delta Z(i) + \delta Z$ . To first order in  $\delta Z$ , this leads to an approximate expression,  $E(\text{corr})(Z(a), Z(b), R) = (\text{partial derivative } E(\text{HF}) / \text{partial derivative } Z(a)) \delta Z(a) + (\text{partial derivative } E(\text{HF}) / \text{partial derivative } Z(b)) \delta Z(b)$ , for the correlation energy based on the charge renormalization parameter  $\delta Z$ , which is fixed systematically from the large- $D$  limit. The theory is applied to diatomic molecules. Near the equilibrium, we are predicting the correlation energy typically with 80% or greater accuracy in a completely self-consistent and systematic way with no additional cost to the Hartree-Fock calculation. An improved approach to estimating the correlation energy for all  $R$  is outlined. (C) 1995 American Institute of Physics.

- [76] R. Bleil and S. Kais. CHARGE RENORMALIZATION AT THE LARGE- $D$  LIMIT FOR ATOMS AND MOLECULES. *Int. J. Quantum Chem.*, pages 349–359, 1995.

**Abstract:** By combining Hartree-Fock results for non-relativistic ground-state energies of atoms and molecules with analytic expressions for the large-dimensional limit of atoms, we obtained a simple systematic renormalization procedure. This procedure is based on the variation of the nuclear charges,  $(Z(i))$ , and internuclear distances,  $(R(ij))$ , of the Hartree-Fock Hamiltonian such that the Hartree-Fock energy will be significantly closer to the exact energy. We calculate to first order in  $\delta Z$  the leading contribution to the correlation energy by changing the nuclear charge to some renormalized nuclear charge,  $Z + \delta Z$ . Our goal is to find the parameter  $\delta Z$  in a completely self-consistent and systematic manner, which we accomplish by utilizing the analytically known solutions for both the exact and Hartree-Fock energies for all atoms in the large- $D$  Limit. We demonstrate that use of the dimensional renormalization parameter  $\delta Z(\text{infinity})$  directly in standard Hartree-Fock calculations for atoms and homonuclear and heteronuclear molecules yields about 2/3 or more of the correlation energy. (C) John Wiley & Sons, Inc.