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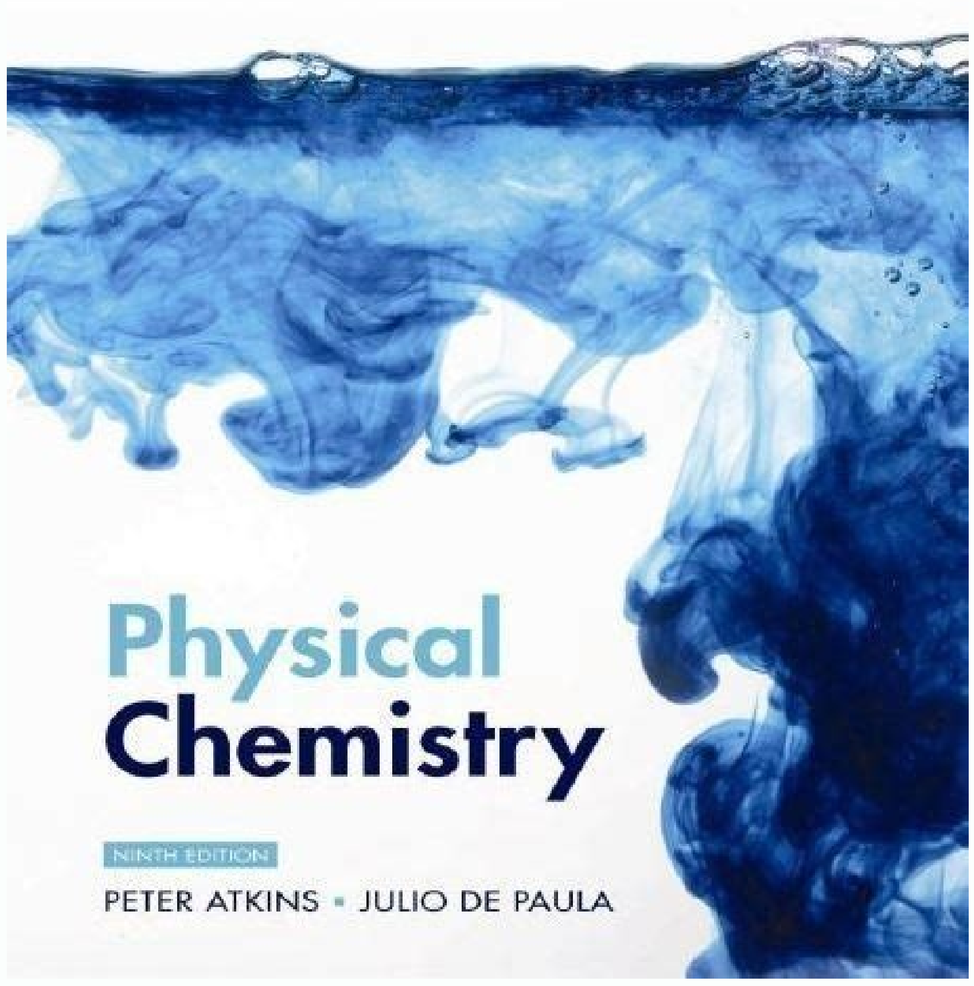

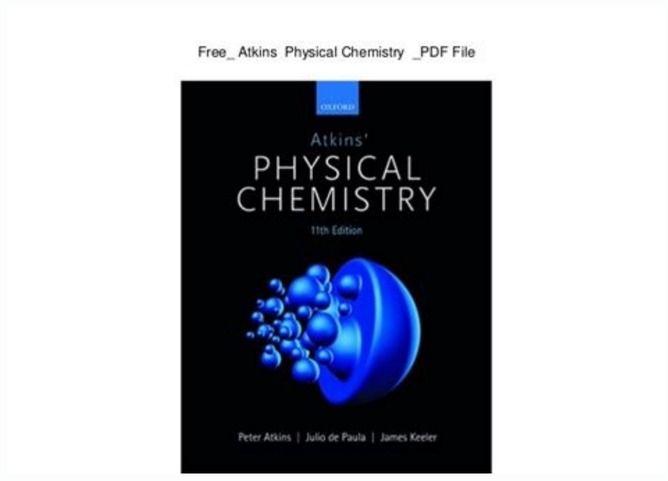

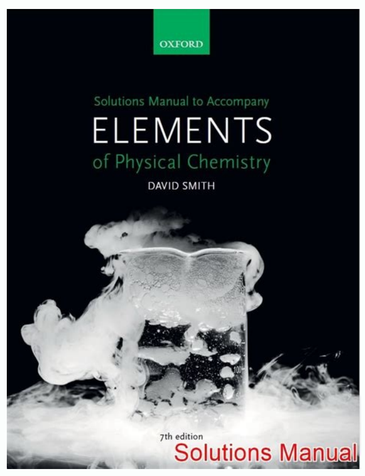

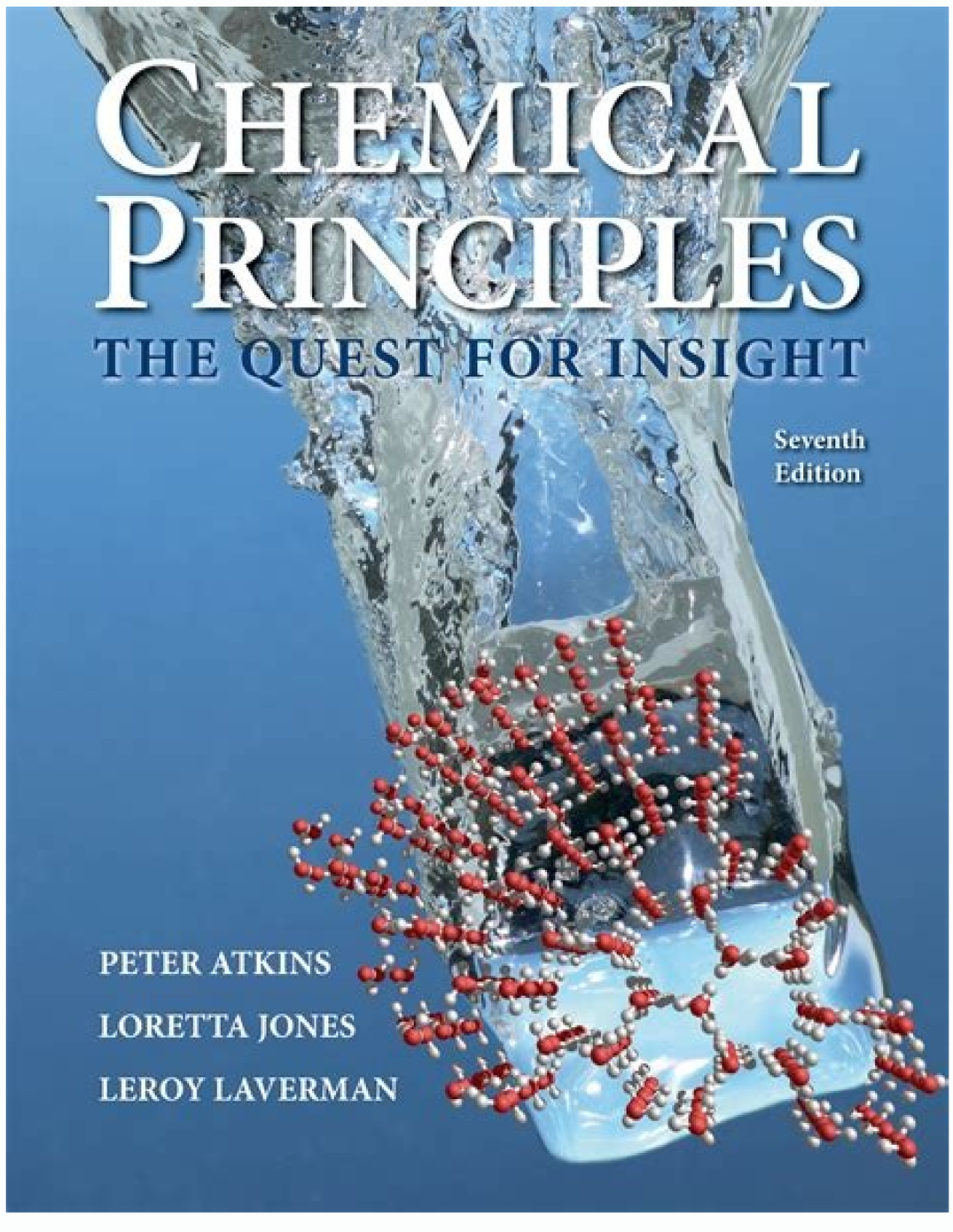

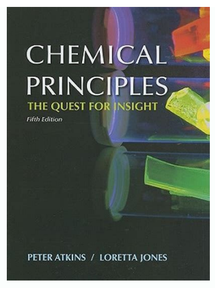

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F.8 F8.1 (a) Units 3 1.45cm3 =1.45 (10- 2 m) = l1.45xl0--{j m 3 I ~)x(~g 1 1 J x(10 g 10 _~mm) 3 3 F8.2(a) (11.2 cm F8.3(a) Pa=Nm- =(Nm)m- =Jm- =lm-3 1 J J J J 2 3 =lll.2x10 kgm- 3 3 1 14 STUDENT SOLUTIONS MANUAL FOR QUANTA, MATTER, AND CHANGE kT F8.4(a) he 23 1 (1.38lxl0- J K-)x(298 K) I _I - - - -34- - - - - -10- - = _207.2 cm 1 . Metalloids typically have the appearance of metals but behave chemically like nonmetals. Ī .. First printing ISBN: 978-0-1995-5907-7 All rights reserved. Averaging/values over the two experiments would yield f values in which the earth's motion is effectively averaged out. An increase in pressure also shifts it to the right so as to reduce the number of moles of gas. F5.6(a) Molecules can survive for long periods without undergoing chemical reaction at low temperatures when few molecules have the requisite speed and corresponding kinetic energy to promote excitation and bond breakage during collisions. You're Reading a Free Preview Pages 22 to 31 are not shown in this preview. (See Fig. (The earth-star direction, which is observable by earth-based astronomers, is practically identical to the sun-star direction, which is technically the direction needed.) Alternatively, repeat the experiment half a year later. So the valence bond approach undervalues any ionic contribution to the trial function by totally neglecting it. Oxidation can result from the loss of the radical electron to form the nitrosyl ion, NO+, which has a bond order equal to 2. , N) =--1 -1-12 (N!) If/a(2)a(2) If/a(l)a(l) If/a(3)a(3) If/a(N)a(N) If/a(2),8(2) If/a(1),8(1) If/a(3),8(3) If/a(N),B(N) lf/b(2)a(2) lf/b(l)a(l) lf/b(3)a(3) lf/b(N)a(N) If/, (2),8(2) lf/z (1),8(1) lf/,(3),8(3) If/, (N),B(N) = -lj/(2, 1, 3, ... r .. Solutions to applications P4.27 The wavenumber of a spectroscopic transition is related to the difference in the relevant energy levels. CaC0 3(s) ~ CaO(s) + C0 2(g) Addition of carbon dioxide shifts the equilibrium to the left. When the central atom has two or more lone pairs, the molecular geometry must minimize repulsion between the relatively diffuse orbitals of each lone pair. e I ...e12---- r .. I ... MATIER, AND CHANGE to bonding of dioxygen with other species such as the atomic radicals Fe(II) of hemoglobin and Cu(II) of the electron transport chain.] = e-(4.97oxw-20 i)1{(us1x10-23 J K-1)x(293 KJ} = 14 .631 x l0-6 1 9 Hlower The ratio Huppe/ Hiower is so small that the population of the upper level is approximately zero. However, the majority of the Exercises and many of the Problems can still be solved with a modem hand-held scientific calculator. The manual is intended for students. These two electrons are unpaired and can contribute 104 STUDENT SOLUTIONS MANUAL FOR QUANTA. Liquids within a vertical, narrow tube exhibit a meniscus that is either concave up or concave down depending on the nature of the attractive or repulsive forces between the liquid and the material of the tube. You're Reading a Free Preview Pages 58 to 83 are not shown in this preview. F3.2(a) (a) (b) (c) (d) Mass is an extensive property. See Sections 5.6--5.9. 05.3 The ion has 24 valence electrons as shown in the Lewis structure. Without the use of these approximations, calculations on polyatomic molecules would have been difficult to accomplish. , ._ ~ ' d "!'~ .·. .... Temperature is an intensive property. You're Reading a Free Preview Page 18 is not shown in this preview. mv 2 F=ma=-r v a= - F6.6(a) 2 r (= 2188xl03 m s- 1)2 53xl0- 12 m = 9.0xl0 22 m s-2 The relationship between angular velocity w and the speed of an electron in a stable circular path (i.e., an "orbit" of radius r) is found by recognizing that, when the electron travels through one orbit, it traverses 2n radians while traveling the distance 2nr. The special size and charge of the Zn 2 + cation makes it useful for the function of some enzymes. Similarly, they component introduces no further constraints, for it involves the same spherical harmonics as the x component. The simple form of the method has three other rather drastic approximations, listed in Section 5.6 of the text, which eliminate many terms from the secular determinant and make it easier to solve. 2 STUDENT SOLUTIONS MANUAL FOR QUANTA, MATIER, AND CHANGE I IA I H 1.008 3 Li 6.941 II Na 22.99 19 K 39.10 2 HA 4 Be 9.012 12 Mg 24.31 20 Ca 40.08 37 Rb 85.47 38 Sr 87.62 55 Cs 132.9 87 Fr (223) 56 Ba 137.3 88 Ra 226 3 1118 4 IVB 5 VB 6 VlB 7 VllB 8 9 lO VIIIB VIHB VIIIB II 18 I 13 IllA 12 llB 14 !VA 15 VA 16 VIA l7 VllA 6 7 N 14.01 15 8 0 9 Periodic Table of the Elements s 21 Sc 44.96 22 Ti 47.88 39 40 Zr 91.22 y 88.91 57 La 138.9 89 Ac (227) F.2 72 Hf 178.5 23 v 50.94 24 Cr 52.00 41 Nb 92.91 73 Ta 180.9 42 Mo 95.94 58 Ce 140.l 90 Th 232.0 59 Pr 140.9 91 Pa (231) 74 w 183.9 25 Mn 54.94 43 Tc (98) 26 Fe 55.85 44 Ru IOI.I 27 Co 58.93 45 Rh 102.9 28 Ni 58.69 29 Cu 63.55 46 Pd 106.4 75 Re 186.2 76 Os 190.2 77 Ir 192.2 78 47 Ag 107.9 79 Au 197.0 60 Nd 144.2 92 u 238.0 Pt 195.l 61 62 63 Pm Sm Eu 145 93 Np 237 150.4 94 Pu (244) 152.0 95 Am (243) B 10.81 13 Al 26.98 31 Ga 69.72 49 In 114.8 81 Tl 204.4 30 Zn 65.38 48 Cd 11::!.4 80 Hg :?00.6 64 Gd 157.3 96 Cm (247) 65 Tb 158.9 97 Bk (247) c 12.01 14 Si 28.09 32 Ge 72.59 50 Sn 118.7 82 Pb 207.2 16.00 16 p s 30.97 33 As 74.92 SI Sb 121.8 83 Bi 209.0 32.07 34 Se 78.96 52 Te 127.6 84 Po (209) F 19.00 17 Cl 35.45 35 Br 79.90 53 I 126.9 85 At (210) 18 VIllA 2 He 4.003 IO Ne 20.18 18 Ar 39.95 36 Kr 83.80 54 Xe 131.3 86 Rn (222) 66 Dy 162.5 98 Cf (251) Molecules F2.1 (a) A single bond is a shared pair of electrons between adjacent atoms within a molecule while a multiple bond involves the sharing of either two pairs of electrons (a double bond) or three pairs of electrons (a triple bond). The hybridizations are (from left to right) sp 2 for the first 0 atom and for the N and sp 3 for the next two 0 atoms. The simple Hiickel method is usually applied only to the calculation of n-electron energies in conjugated organic systems. Many of the problems specifically requested the use of such software, and, indeed, would have been almost unsolvable otherwise. 5 The chemical bond Answers to discussion questions 05.1 Our comparison of the two theories will focus on the manner of construction of the trial wavefunctions for the hydrogen molecule in the simplest versions of both theories. (b) Xenon tetrafluoride, XeF4 •F • · 1 / " ·.. We would be grateful to any readers who bring any remaining errors to our attention. (See Chapter 7.) 05.9 See Impact 15.1 for a more detailed discussion. ume.)=A At Xmin the harmonic oscillator restoration force (Hooke's law, -kx) is zero, and consequently, the harmonic potential energy, V, is a minimum that is taken to equal zero while kinetic energy, Ek> is a maximum. 19 M = Eupper -E10wer = 1 eV = 1.6022xl0- J F5.2(a) (a) (b) Hupper = e - llE / kT = e-(1.6022xl0-19 i)t{(l.381xl0-23 JK-l)x(3000 KJ} = l2.092 x 10-2 I Hlower F5.3(a) lim(Hupper)=lim(e-w*r) [F.9]=e- =0 Hlower T ->0 T ->0 In the limit of the absolute zero of temperature all particles occupy the lower state. When sufficient though not excessively large energy is available, biological processes can channel an electron into this HOMO to produce the reactive superoxide anion of bond order 11/ 2. It has a density compatible with the close proximity of either its constituent elemental atoms or its constituent molecules, and consequently it has low compressibility. FUNDAMENTALS F3.3(a) F3.4(a) ~ = 25.0 g(1 mo!) = lo.543 moll 46.069 g (a) n= (b) 6 0221 1023 x molecules] = l3.27xl0 23 molecules I N = nNA = 0.543 mo1 (· mo! (a) m=nM=lO.Omol ((b) weight= F gravityonEanh = m g M F mg A A [P.l] 18.015g) ~ =~ mo! [P.l] Eanh = (180. This is Postulate IV of the text. F--xe-F I Orientations caused by repulsions between three lone pairs and two bonding pairs: F . Consequently, the equipartition theorem assigns a mean energy of 3/ 2kT to each atom. , N) Only the null function satisfies a relationship in which it is the negative of itself so we conclude that, since the null function is inconsistent with existence, the Slater determinant satisfies the Pauli Exclusion Principle [Section 4.4 b]. Rows 1 and 2 are identical in the Slater wavefunction below. Eleventh Edition Peter Bolgar, Haydn Lloyd, Aimee North, Vladimiras Oleinikovas, Stephanie Smith, and James Keeler July 2018 ISBN: 9780198807773 736 pages Paperback 246x189mm In Stock Price: £39.99 The Student Solutions Manual to accompany Atkins' Physical Chemistry 11th Edition provides full worked solutions to the 'a' exercises, and the odd-numbered discussion questions and problems presented in the parent book. They either completely give up their energy or they are not absorbed. Special biological or industrial processes are needed to channel energy for promotion of 2crelectrons into high-energy, reactive states. 5.22 that defines the Pauling scale. Gases are compressible. C.G. Contents Fundamentals PART1 Quantum theory 5 15 The chemical bond Answers to discussion questions Solutions to exercises 1 The principles of quantum theory 17 Solutions to problems Solutions to numerical problems Answers to discussion questions Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to applications 17 18 26 26 28 31 Solutions to theoretical problems Solutions to applications Nanosystems 1 : motion in one dimension Answers to discussion questions Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to applications 33 33 34 43 43 45 52 132 Answers to discussion questions Solutions to applications 132 133 143 143 146 154 Molecular symmetry 156 Solutions to problems Solutions to numerical problems Solutions to theoretical problems 7 Solutions to applications 156 156 162 162 173 8 Molecular assemblies 176 Answers to discussion questions 176 179 185 185 193 Answers to discussion questions 3 Nanosystems 2: motion in several dimensions Solutions to exercises 55 Solutions to problems Solutions to numerical problems Answers to discussion questions 55 Solutions to exercises 55 Solutions to problems Solutions to theoretical problems 62 62 66 Solutions to applications 72 Solutions to numerical problems Solutions to exercises Solutions to problems PART2 4 Atoms, molecules, and assemblies Atomic structure and atomic spectra Answers to discussion questions Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to applications Solutions to numerical problems 77 79 79 80 88 88 92 98 102 104 110 110 124 128 Computational chemistry 6 Solutions to exercises 2 102 Solutions to applications 9 Solids Answers to discussion questions Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to applications 196 196 198 207 207 210 221 viii CONTENTS PART3 Molecular spectroscopy 225 10 Rotational and vibrational spectra 227 Answers to discussion questions 227 228 236 236 244 247 Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to applications 11 Electronic spectroscopy 251 15 The second law of thermodynamics 352 352 354 364 364 374 382 Answers to discussion questions Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to applications 16 Physical equilibria 385 Answers to discussion questions Solutions to applications 385 386 395 395 401 406 Solutions to applications 251 253 261 261 265 267 Solutions to exercises 12 Magnetic resonance 271 17 Chemical equilibrium 411 Answers to discussion questions 271 272 279 279 284 286 Answers to discussion questions 411 413 422 422 433 Answers to discussion questions Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to thermodynamics Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to applications PART5 Chemical dynamics 289 18 Molecular motion 441 Answers to discussion questions 441 443 454 454 459 466 13 The Boltzmann distribution 291 Answers to discussion questions 291 292 304 304 308 311 Solutions to exercises 14 The first law of thermodynamics 314 19 Chemical kinetics Answers to discussion questions 314 315 326 326 335 348 Answers to discussion Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to applications Solutions to exercises Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to applications 439 Solutions to problems Solutions to numerical problems Solutions to theoretical problems Solutions to applications 469 quest1o~s 469 472 479 479 486 489 Solutions to exercises Solutions to problems Solutions to numerical problem> Solutions to theoretical pr Solutions to applications i·~~-. 01 .5 By wave-particle duality we mean that in some experiments an entity behaves as a wave while in other experiments the same entity behaves as a particle. Z electrons occupy atomic orbitals, which are voluminous regions of the atom that describe where electrons are likely to be found with no more than two electrons in any orbital. The next bond is a cr bond involving Nsp 2 and Osp 3 orbitals. r=, g dt !=0 v(t) =gt (a) v(l.O s)=(9.81 ms-2)x(l.O s)=l9.81 ms- 1 1 (b) v(3.0 s) = (9.81 m s-2)x(3.0s)=129.4 m s- 1 I ~ =tmv2 =t(0.0010kg)x(29.4ms- 1 }2 =I0.43JI F6.2(a) The terminal velocity occurs when there is a balance between the force exerted by the electric field and the force of frictional drag. F6.4(a) The harmonic oscillator solution x(t) =A sin(wt) has the characteristics x(t) = Asin(wt)+Bcos(wt) dx v(t) = dt x min = Awcos(wt) =x(t=nn l w, n=0, 1,2... Nonmetals do not conduct electricity and are neither malleable nor ductile. kJmo1- (b) 1 I 6 626 10 34 1 till= · x s = l3.3xl0-34 JI, lo.20 nJ mo1- 1I 2.0 s This is much too small to be measurable, thereby, demonstrating that for practical purposes the energy of a macroscopic object is a non-quantized, continuous variable. 1.16. ·~ F-Xe-F I °F F Orientations caused by repulsions between two lone pairs and four bonding pairs: Molecular shape: square planar with 90° bond angles (b) P - H F2.5(a) Nonpolar or weakly polar. The first bond is a double bond whose cr component arises from the overlap of sp2 orbitals and whose 7r: component comes from overlap of unhybridized p orbitals. Photons are never partially absorbed. xl0_19 JI 3 37 590xl0-9 m where the period T equals 1I v (T = 1I v) till= 6.626xlo-34 J s = 3.3x10-20 J = J33 zJI 2ox10- 15 s This corresponds to NA x(3 .3xl0-20 J)=120. You're Reading a Free Preview Pages 145 to 148 are not shown in this preview. A shell consists of n2 individual orbitals, which are grouped together into n subshells. Solutions to exercises he till=hv [1.1]=- E1.1(a) IL = (6.626xl0- E1 .2(a) till = hv = h I T (a) 34 8 1 J s)x(2.998xl0 ms-)=1 . For all neutral atoms other than hydrogen, the subshells of a given shell have slightly different energies. Whenever the system is described by a wavefunction If/, which is an eigenfunction of fl, the outcome of a measurement of the observable Q will be the eigenvalue w. In order to distinguish between them, we need to carry lots of significant figures in the calculation. The molar internal energy is Um =%NakT = 3RT [F.IO] = 3(8.3145 J mol- 1 K- 1)(293 K) = 7.31 kJ mol- 1 7 31 U = nUm = mM- 1Um = (10.0 g)(l mo! J(· kJ)=14.56 kJI 16.04 g mo! FUNDAMENTALS 9 F5.11 (a) See Exercise F5 .9(a) for the description of the molar internal energy of argon. We warmly thank our publishers, especially Jonathan Crowe and Jessica Fiorillo, and also Samantha Calamari, for their patience in guiding this complex, detailed project to completion. Molecular orbital theory explains both these obstacles by assigning N2 a configuration that gives rise to a high bond order (triple bond) with all electrons paired. (3) Neutron and electron diffraction studies indicated that these particles also possess wave-like properties of constructive and destructive interference. Blundell, Roberto De Renzi, Tom Lancaster, Francis L. dV = -Fxdx [F.20] = kx dx (i.e., Fx = -kx; Exercise F6.3a) r x> dV r kxdx = V(x) = tkx F6.5(a) 2 Thus, vmax 2 2 = V(xm.J = 1kA and IE= vmax = tkA I The electron acceleration is caused by the centripetal electrostatic force of attraction of the positively charged nucleus for the negatively charged electron. So the molecular orbital approach greatly overvalues the ionic contributions. F5.12(a) See Exercise F5.10(a) for the description of the molar internal energies of carbon dioxide and methane. P. All knowledge of the linear momentum of the particle is lost when its position is specified exactly. F5.7(a) Vmeanoc(T / M)" 2 [F.11] Vmean (T2) (T2/ M)l/2 =(T2J112 VmeaJz;) (I; ! M}' 12 I; 112 Vmean (313 K) =(313 K) Vmean (273K) 273K F5.8(a) Vmean oc (T / M)' 2 =l1.07I [F.11] 12 vmea0 (N 2) = (44.0gmor:J ' =11.2 5 1 vmean (co2) 28.0 g mor F5.9(a) A gaseous argon atom has three translational degrees of freedom (the components of motion in the x, y, and z directions). Molecular nitrogen is very stable in most biological organisms, and as a result the task of converting plentiful atmospheric N2 to the fixed forms of nitrogen that can be incorporated into proteins is a difficult one. In the valence bond method, the trial function is a linear combination of two simple product wavefunctions, in which one electron resides totally in an atomic orbital on atom A and the other totally in an orbital on atom B. 5.22 (the Pauling scale), we see that if D(A-B) were equal to 1/ 2 [D(A-A) + D(B-B)], the calculated electronegativity difference would be zero, as expected for completely non-polar bonds. Iggo, Konstantin Luzyanin Request an Inspection Copy Second Edition Gareth Price Request an Inspection Copy Second Edition Wai-Kee Li, Hung Kay Lee, Dennis Kee Pui Ng, Yu-San Cheung, Kendrew Kin Wah Mak, Thomas Chung Wai Mak Request an Inspection Copy Second Edition Wai-Kee Li, Hung Kay Lee, Dennis Kee Pui Ng, Yu-San Cheung, Kendrew Kin Wah Mak, Thomas Chung Wai Mak Request an Inspection Copy Second Edition Wai-Kee Li, Hung Kay Lee, Dennis Kee Pui Ng, Yu-San Cheung, Kendrew Kin Wah Mak, Thomas Chung Wai Mak Request an Inspection Copy Student Solutions Manual to Accompany Quanta, Matter, and Change A molecular approach to physical chemistry Charles Trapp, Marshall Cady, Carmen Giunta STUDENT SOLUTIONS MANUAL FOR QUANTA, MATTER, AND CHANGE: A MOLECULAR APPROACH TO PHYSICAL CHEMISTRY C. Trapp, M. You're Reading a Free Preview Pages 35 to 42 are not shown in this preview. Interchanging these two rows causes the sign to change without in any way changing the determinant. We are given wavelength data, so we can use 100 STUDENT SOLUTIONS MANUAL FOR QUANTA, MATIER, AND CHANGE The ratios are 438 392 · run = 0.998884, 438.882 nm 440 510 44 · run = 0.998889, and 1.5 l O nm = 0.998846 441.000 nm 442.020 nm The fre uencies of the stellar lines are all less than those of the stationary lines, so we infer that the star is receding from earth. If we look at eqn. To the far right (Cu and Zn), effective nuclear charge may be higher but there are few, if any, orbitals available for bonding. If/a(l)a(l) If/a(2)a(2) If/a(3)a(3) If/a(N)a(N) If/a(l)a(l) 1 lf/(l, 2, 3, ... The electrostatic attraction binds the negatively charged electrons to the positively charged nucleus, and the so-called strong interaction binds the protons and neutrons within the nucleus. Solutions to exercises ES.1 (a) The valence bond description of P2 is similar to that of N2, a triple bond. AND C'-'- FS.S(a) Kinetic molecular theory, a model for a perfect gas. Ease of solution was important in the early days of quantum chemistry before the advent of computers. • , . 11UH,o =energy dissipated by the electric circuit =I 11rp l1t [F.30) = (2.23 A)x(15.0 V)x(720 s) = 24. F5.4(a) M = Eupper - E 10wer = vhc = (2500 cm- ')(6.626x 10-34 J s)(3.000xl0 10 cm s- 1) = 4.970x10- 20 J Hupper = e-llE t klT [F. lxl0 3 C s- 1 Vs= 124.1 kJI 11UH,o = (nC!1T)H,o [F.5) 11T = 11U H,O (nC)H,o 24.lxl0 3 J (200 g)x(75.3 J K- 1 mor 1) I (18.02 g mor 1) /1UH,O (mC I M)H,o = 28.8K=128.8 °cl F.7 F7.1(a) Waves Ji=_!_ [F.33)= A, 2 1 (io- mJ=ll.69xl0 4 cm- 11 9 590xl0- m cm v=~ 8 [F.31]= 3 .00xl0 ms-I =5.08xl0 14 s- 1 =l5 .08x10 14 Hzl A, 590x10-9 m = !!... [F.32) = 3.00xlOs m s-1 = l2.26x10s m s-1I n, 1.33 F7.2(a) cH o F7.3(a) A=~v [F.33)= 25001cm_1(10 ' 106 2 µmJ=14.00 µml cm v = ~ [F.31) = 3.00xl0 ms-' = 7.50xl0 13 s- 1 = l7.50xl0 13 Hzl 8 A, F7.4(a) 4.00xl0-6 m (a) j(x) = cos(2nx/},) where).= 1 cm (See Figure F. Get a copy of Solution Manual Physical Chemistry 7th Edition by Atkins P., de Paula J. 01 .3 If the wavefunction describing the linear momentum of a particle is precisely known, the particle has a definite state of linear momentum; but then according to the uncertainty principle (eqn. l.19a and 1.23). To obtain numerical values for individual atoms, a reference state (atom) for electronegativity must be established. The force and its resultant acceleration always point from the electron to the nucleus. as .. Consequences are especially important for small fundamental particles like electrons, atoms, and molecules. The tendency of Fe 2 + and Cu+ to bind oxygen proves very useful in hemoglobin and electron transport (respiratory) chain, respectively. Alternatively, resonance structures may be drawn and, if desired, formal charges (shown in circles below) may be indicated. The energy integrals, aand /3, are always considered to be adjustable parameters; their numerical values emerge only at the end of the calculation by comparison to experimental energies. It is not possible to precisely specify complementary observables like position and momentum for fundamental particles. The readily available +2 and +3 oxidation states of Mn, Fe, and the +1 and +2 oxidation states of Cu make these cations useful in electron transfer processes occurring in chains of specialized proteins within biological cells. You're Reading a Free Preview Pages 267 to 298 are not shown in this preview. But the requirement of the superposition of an infinite number of momentum wavefunctions in order to locate the particle means a complete lack of knowledge of the momentum. This phenomenon is related to the availability of both electrons and orbitals favorable for bonding. Solids may be characterized by terms such as brittle, ductile, tensile strength, toughness, and hardness. This means that an atom or molecule has specific, allowed energy levels, and we say that their energies are quantized. In the simplest version of the method, the overlap integral is also parameterized. 5.29, 5.31, and 5.34 of the text. You're Reading a Free Preview Pages 159 to 194 are not shown in this preview. H. , N) = - -1-12 lf/b(l)a(l) (N!) : If/a(2)a(2) If/a(3)a(3) If/a(N)a(N) lf/b (2)a(2) lf/b(3)a(3) lf/b(N)a(N) lf/z (1),8(1) lf/z (2),8(2) lf/z(3),8(3) If/=(N),B(N) = -lf/(2, 1,3, ... The whole set of selection rules, then, is that transitions are allowed only if IM= ±1 and !:1m =0 or±ll 1 P4.25 (a) The Slater wavefunction [4.32) is lf/(1,2,3, ...,N) 1 =-(N!) 112 If/a(1)a(l) If/a(2)a(2) If/a(3)a(3) lf/a(N)a(N) If/a(1),8(1) If/a(2),8(2) If/a (3) ,8(3) If/a(N),B(N) lf/b (1)a(l) lf/b(2)a(2) lf/b(3)a(3) lf/b(N)a(N) If/, (1) ,8(1) lf/z(2),8(2) lf/z(3),8(3) If/, (N),B(N) Interchanging any two columns or rows leaves the function unchanged except for a change in sign. Electrons behave as waves in diffraction experiments but as particles in the photoelectric effect. 05.5 Both the Pauling and Mulliken methods for measuring the attracting power of atoms for electrons seem to make good chemical sense. Gases have no fixed shape or volume. SF4 is a seesaw molecule, and it is a polar molecule. :o-s-o: :O-s-o: :o-s-o: .. Published in the United States and Canada by W. This causes constituents to be placed randomly in contrast to the orderly array in crystals. Shaded versus unshaded atomic-orbital (AO) lobes represent opposite signs of the wave funcstions. is the displacement from equilibrium (a) w=t(450Nm- 1)x(1ox10- 12 mf =2.25x10-20 Nm= l2.25x10-20 JI (b) w=t(450Nm- 1)x(2ox10- 12 m}2 =9.00x10-20 Nm= 19.00xl0-20 JI F6.8(a) 2 t mv 2 = efirp or V = 2emfirp)" (19 v = 2(1.6022x10- c)x(1ooxl0 (9.10938xl0-3 1 kg =1.ssx10 8 (kg~: s- 2 3 v)]" 2 vJ" 2 (c = 1.88xl0 kg 8 J" 2 = 1.88xl0 8 (J kg 2 J" =li.ssx1os ms- 1 1 , E =Ek = efirp = ex(lOO kV)= 1100 keVI F6.9(a) The work needed to separate two ions to infinity is identical to the Coulomb potential drop that occurs when the two ions are brought from an infinite separation, where the interaction potential equals zero, to a separation of r. The constituent molecules move freely and randomly. (5) The heat capacities of monatomic solids such as copper metal. Rather, the wavefunction is a superposition of many wavefunctions, each corresponding to a different value for the linear momentum. © C. The magnitude of the centripetal acceleration is found by equating the force of Newton' s second law of motion and the centrifugal force. 5.7, one for each electron: l/f = [A(l) ± B(l)][A(2) ± B(2)] = A(l)A(2) + B(l)B(2) + A(l)B(2) + B(l)A(2) This function gives as much weight to the ionic forms as to the covalent forms. Enquiries concerning reproduction outside those terms and in other countries should be sent to the Rights Department, Oxford University Press at the address above. Consequently, the equipartition theorem assigns a mean energy of 5/ 2kT to each molecule. F4.1 O(a) In a state of dynamic equilibrium, which is the character of all chemical equilibria, the forward and reverse reactions are occurring at the same rate and there is no net tendency to change in either direction. The solutions were carefully cross-checked for errors not only by us, but very thoroughly by Valerie Walters, who also made many helpful suggestions for improving the solutions. Elements to the left (Sc and Ti) of the series have few electrons, and a relatively low effective nuclear charge leaves d orbitals at high energies that are relatively unsuitable for bonding. E1 .3(a) v={ ~e xEk 112 } 0 0 and spherical harmonics Yi,m,: r:,1and the other r;,_1. Grou Oxidation State 0 +l +2 +3 +4 +5 +6 +7 3 Sc 4 5 Ti v 6 Cr 3d 4s- 3d 4s Q Q Q Q Q Q Q Q 7 Mn Q Q Q 8 Fe 9 Co Ni 11 Cu 3d 4s 3d 4s 3d 1 4s Q Q Q Q Q 10 12 Zn G Toward the middle of the first transition series (Cr, Mn, and Fe), elements exhibit the widest ranges of oxidation states. 19 l.6022xl0- C (1 rp= 4tr(8.85419xl0- 12 r 1 C 2 m- 1) 2oox10- 12 m = -2.40 J c- 1 = -2.40 c F6.11 (a) 1) 150x10- 12 m v c- 1 = l-2.40 vi We will assume that the electric circuit has a negligibly small heat capacity so that the water receives all of the electrically generated heat energy. Number density is an intensive property. You're Reading a Free Preview Pages 513 to 514 are not shown in this preview. max = .!.m v max = .!.mA w 2 2 2 where w= (k I m) 112 or mw2 = k We begin the analysis that uses Xm ax by deriving the expression for the harmonic potential energy. (b) The possibility that two electrons occupy the same orbital with the same spin can be explored by making any two rows of the Slater determinant identical, thereby providing identical orbital and spin functions to two rows. , N) This demonstrates that a Slater determinant is antisymmetric under particle exchange. The energy of a photon can be calculated if either the radiation frequency or wavelength is known: Ephoton =hv = hcl,J... Like a solid, it has a density caused by the close proximity of either its constituent elemental atoms or its constituent molecules, and it has low compressibility. Conversely, if the position of a particle is precisely known, its linear momentum cannot be described by a single wavefunction. A path of constant radius r is possible only when the electron speed v creates a centrifugal force, mv2/r, that exactly balances the centripetal force. J = 127.2 Kor 27.2 3.67 J K- 1 °CI 1 mo! J = 0.483 mo! 207.2 g t:,,.U = Ct:,,.T [F.5] = nCmt:,,.T = (0.483 mo!)(26.44 J K- 1 mol- 1)(10.0K)=1128 JI F4.3(a) F4.4(a) FUNDAMENTALS F4.5(a) 7 Dividing eqn. 1 (6.626xl0- J s)x(2.998xl0 cm s-) F8.5(a) 3 44 1 1 8.3l)x(Pa m)x(atm (K mol J 101325 Pa F8.6(a) (1 dmJ atm)x(10-1 m)J x(l01325 Pa)x(-J-)=1101.325 Jj elm 1 atm Pam3 F8.7(a) (a) 2 Base unit of~= (Eor (b) Unit of __i__2 = E0 r (C 2 c2 J _ 2 C1 I)x(~) 10-1 m 3 = lo.08206 atm dm 3 K- 1 moi- 1l c2 1 (kg m2 s-2) 2 _) ( ) = (J m-)x = lkg m s- 1 m I x m2 J r 1 m-)x(m2) 2 = (J m- 1)x(kg ~ 8 2 -) =kg m s-2 = lIiJ PART 1 Quantum theory 1 The principles of quantum theory Answers to discussion questions 01 .1 At the end of the nineteenth century and the beginning of the twentieth, there were many experimental results on the properties of matter and radiation that could not be explained on the basis of established physical principles and theories. 1.17 turns into the sharply spiked packet shown in Fig. I ·~xe--: .~I F Molecular shape: linear with a 180° bond angle 4 STUDENT SOLUTIONS MANUAL FOR QUANTA, MATTER, AND CHANGE (d) XeF4 Lewis structure: /-. 5 .31 of the text.) Dioxygen is kinetically stable because of a bond order equal to two and a high effective nuclear charge that causes the MOs to have relatively low energy. 01 .7 (a) The eigenvalue equation Qlj/ = QJlf/ provides the relation between the operator for an observable (fl) and the value of the observable (w). 5.1 and 5.2, as well as Fig. Peter Bolgar, Recent graduate from the Department of Chemistry, University of Cambridge, Haydn Lloyd, Recent graduate from the Department of Chemistry, University of Cambridge, Aimee North, Recent graduate from the Department of Chemistry, University of Cambridge, Vladimiras Oleinikovas, Recent graduate from the Department of Chemistry, Stephanie Smith, Teaching Fellow in the Department of Chemistry, University of Cambridge, and a Bye Fellow of Pembroke College, Cambridge, and James Keeler, Senior Lecturer in Chemistry at the University of Cambridge and Walters Fellow in Chemistry of Selwyn College, Cambridge. In general we adhered rigorously to the rules for significant figures in displaying the final answers. The upper state is empty. There is a total of five quadratic degrees of freedom for the molecule. Liquids are characterized by terms such as surface tension, viscosity, and capillary action. 12.. The acceleration of free fall is constant near the surface of the Earth. The molecular orbital function for the hydrogen molecule is a product of two functions of the form of eqn. F2.4(a) Molecular shape and polyatomic ion shape are predicted by drawing the Lewis structure and applying the concepts of VSEPR theory. Freeman and Company 41 Madison Avenue New York, NY 10010 www.whfreeman.com ISBN-10: 1-4292-2375-8 ISBN-13: 978-1-4292-2375-1 British Library Cataloguing in Publication Data Data available Preface This manual provides detailed solutions to all of the end-of-chapter (a) Exercises, and to the odd-numbered Discussion Questions and Problems in Quanta, Matter, and Change. For a one-electron atom or ion, the relationship is ATOMIC STRUCTURE AND ATOMIC SPECTRA 99 v, using the definition tz = h l 27r and the fact that Z = 2 Solving for 4 for He, yields J4iee (1 v = 2c 2 h 3 c _ 0 -;;z--;;z1) 2 l Note that the wavenumbers are proportional to the reduced mass, which is very close to the mass of the electron for both isotopes. Thus, w= vx(2n / 2nr) = v I r FUNDAMENTALS 2 J=lm=(mr)x(;) =mrv 11 [F.15) = (9.10938xl0-3 1 kg)x(53x10- 12 m)x(2188xl0 3 m s- 1) = 1.lxl0-34 J s 2 = (1.1x10-34 J s) x (;) 1i 34 =(l.lxl0- Js)x(F6.7(a) w = t kx 2 where 1i = h I 21£ 2 1£_)n=ll.onl 6.63x10 34 J s where x = R - R. Consequently, we conclude thatf(x,t) satisfies the wave equation. The molar internal energy is um= f NAkT = f RT [F.10] = f(8.3145 J mol-I K- 1)(293 K) = 6.09 kJ mor 1 1 U = nU"' = mM- Um = (10.0 g{ ~4~0~ J(6 :·0 ~1) = ll.38 kJJ (b) A gaseous, nonlinear methane molecule has three quadratic translational degrees of freedom (the components of motion in the x, y, and z directions) and three quadratic rotational degrees of freedom . I(} I °C = %X(BFI BF/ 0 P = 0 P - 32) or BFI 0 P = %X(} I °C + 321 ;%' xB /°C + 32 = %x78.5+32=173 l(}F = 173 opl 6 STUDENT SOLUTIONS MANUAL FOR QUANTA, MATIER, AND CHANGE (7.0+273.15)K) = I105 kPa I [(20.0+273.15) K F3.10(a) 110 kPa x F3.11 (a) mRT pV = nRT [F.3] = - M M = mRT = pRT pV = where p is the mass density p (3.710 kg m-3)(8.314 J K- 1 mor 1)(773.15 K) 3 93 .2x10 Pa = 0.256 kg mol-I = 256 g mor 1 The molecular mass is eight times as large as the atomic mass of sulfur (32.06 g mor 1), so the molecular formula is ~. P4.31 Electronic configurations of neutral, 4th-period transition atoms in the ground state are summarized in the following table along with observed positive oxidation states. It is also impossible to specify the simultaneous energy and timing of an event. The fact that N2 possesses no unpaired electrons is itself an obstacle to facile reactivity, and the great strength (large dissociation energy) of the N2 bond is another obstacle. Giunta, 2009 The moral rights of the author have been asserted. A relatively large AO represents the major contribution to the MO. Thus, compared to the HOMO of dioxygen, the one electron of the 27r HOMO is a high-energy, reactive radical. Additionally, the HOMO, being antibonding and predominantly centered on the nitrogen atom, is expected to bond through the nitrogen. Giunta Professor of Chemistry, Le Moyne College, Syracuse, NY, USA OXFORD UNIVERSITY PRESS OXFORD UNIV E RSI TY PRESS Oxford University Press, Great Clarendon Street, Oxford, OX2 6DP, United Kingdom Oxford is a registered trade mark of Oxford University Press in the UK and in certain other countries. ·~. C. The resulting positions of attached atoms (not lone pairs) are used to classify the shape of the molecule. N20 is a linear, polar molecule. In the limit of an infinite number of superposed wavefunctions, the wavepacket illustrated in text Fig. As a result, 0 2 is very reactive in biological systems in ways that promote function (such as respiration) and in ways that disrupt it (damaging cells). This is Postulate Vkofthe text. The electric potential will be calculated along the line of the ions. You're Reading a Free Preview Pages 320 to 491 are not shown in this preview. Furthermore, it is assumed that the repulsion between a lone pair and a bonding pair is stronger than the repulsion between two bonding pairs, thereby making bond angles smaller than the idealized bond angles that appear in the absence of a lone pair. I : - - - - - - - .) (b) j(x) = cos(2n:x/). This is a very crude approximation and works best when the energy level pattern is determined largely by the symmetry of the molecule. cm3 10-6 m3 = l.8 x l0 6 Pa= li.8 MPal ~' F3.13(a) = 1.0 mole _

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