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Rotational *g* factors calculated for diatomic molecular cations H₂⁺, HeH⁺ and NeH⁺

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Abstract

For three diatomic molecular cations— H_2^+ , HeH⁺ and NeH⁺ and their isotopic variants, we calculated the rotational *g* factor, g_r , as a function of internuclear separation *R* with attention to characteristics at distances much smaller or larger than equilibrium separation R_e and with the correct nuclear contribution in terms of nuclear masses. We derive a general limiting formula for g_r at large internuclear separations: $g_r \rightarrow m_p \mu M_b^{-2}$, in which μ is the molecular reduced mass and M_b is the mass of the separating cation, both in terms of atomic masses, and m_p is the protonic rest mass.

1. Introduction

The rotational g factor, g_r , arises as a significant parameter of proportionality between the density of magnetic flux applied to a gaseous sample and the consequent splitting of lines in the pure rotational spectrum. We have collected elsewhere [1] much information from experiments and calculations about g_r of diatomic molecules in their ground electronic state $X^1\Sigma^+$. Within a context of treating separately the electronic and nuclear motions relative to axes fixed in a particular molecular frame, one expresses this quantity as a radial function $g_r(R)$ of internuclear separation R; experimental observations relate to appropriate expectation values $\langle vJ|g_r(R)|vJ\rangle$, or their differences, for various vibrational and rotational states, in terms of quantum numbers v and J respectively. For molecular ions the available values [1] of g_r pertain to typically the equilibrium internuclear separation, R_e , from calculation or the ground vibrational state for experiment, except for HeH⁺ for which calculations have produced values of g_r for internuclear distance over a broad range [2]. For H⁺₂ of electronic ground state $X^2\Sigma_g^+$, calculations yielded values over a small range near R_e [3]; those values were applied to calculate the expectation values $\langle v|g_r(R)|v\rangle$ for vibrational states up to v = 10 [4].

For known neutral diatomic molecules $g_r(R)$ approaches zero as $R \to \infty$, but for HeH⁺ this behaviour was contraindicated [2]. For practical purposes concerned with modelling radial

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functions that occur in an effective Hamiltonian for nuclear motion [5], one seeks knowledge about not only the limiting values of pertinent quantities towards limits of united atom and separate atoms from a diatomic molecule but also the dependence on internuclear distance in the approach to these limits. Such knowledge is known about the internuclear potential energy and electric dipolar moment [6], for instance, and extension to other pertinent quantities is clearly desirable. For this reason we have calculated $g_r(R)$ for R over a large range for several diatomic molecular species, both neutral and ionic; we discuss here our results for molecular ions and their analysis that has yielded a general formula applicable at large distances.

2. Theory

As an extensive treatment of molecular magnetic quantities and their relation to an effective Hamiltonian has appeared elsewhere [1, 7], we present here only a summary of relevant concepts and equations. Measurements of rotational *g* factors of isotopic variants exhibit a strong dependence on nuclear mass; for this reason and because of the way that a nuclear contribution arises in changing from nuclear masses to atomic masses in the production of an effective molecular Hamiltonian [5], we express the rotational *g* factor of a diatomic molecular species as a sum of nuclear and electronic contributions,

$$g_{\rm r}(R) = g_{\rm r}^{\rm nu}(R) + g_{\rm r}^{\rm el}(R).$$
 (1)

The nuclear contribution depends on only atomic numbers and nuclear masses [5],

$$g_{\rm r}^{\rm nu} = m_{\rm p} (Z_{\rm a} m_{\rm b} / m_{\rm a} + Z_{\rm b} m_{\rm a} / m_{\rm b}) / (m_{\rm a} + m_{\rm b})$$
(2)

and is thus independent of internuclear distance; here m_p , m_a and m_b are the rest masses of a proton and of the nuclei of atomic centres A and B, respectively; Z_a and Z_b are the corresponding atomic numbers. The electronic contribution $g_r^{el}(R)$ is a sum, weighted by energy, of electronic matrix elements [1] between the state of interest, here the electronic ground state of symmetry class ${}^{2}\Sigma_{g}^{+}$ for H_{2}^{+} and ${}^{1}\Sigma^{+}$ for HeH⁺ and NeH⁺, and electronically excited states of symmetry class Π , and depends strongly on internuclear distance. For a molecule of relative polarity ${}^{-}AB^{+}$, the total rotational g factor partitions into contributions of an *irreducible* part and another part related to the electric dipolar moment [5, 7]:

$$g_{\rm r}(R) = m_{\rm p} \left\{ g_{\rm r}^{\rm irr}(R)/\mu - p(R)[1/M_{\rm a} - 1/M_{\rm b}]/eR - \frac{1}{2}\mu Q \left[1/M_{\rm a}^2 + 1/M_{\rm b}^2 \right] \right\}.$$
 (3)

Here $g_r^{irr}(R)$ represents irreducible nonadiabatic rotational effects essentially independent of atomic masses, related to the electronic matrix elements mentioned above, p(R) is a radial function for molecular electric dipolar moment, and $Q = Z_a + Z_b - n$ is the net charge number for a molecular ion with *n* being the total number of electrons; for molecular cations of interest in the present work, Q = +1. Therein appear also the fundamental unit of electric charge *e*, and the molecular reduced mass $\mu = M_a M_b/(M_a + M_b)$; the latter quantity comprises a product of atomic masses M_a and M_b of constituent atoms divided by their sum no matter whether the molecule dissociates into neutral atoms or atomic ions [5, 7]. As information about the nature of mass effects is important in assessing the behaviour of these radial functions, we recall also a relation [5] between the rotational *g* factor $g_r(R)$ of a standard species for a particular molecular entity and $g_r(R)'$ of an isotopic variant; primed quantities denote properties of an isotopic variant thereof with its atomic reduced mass μ' and its constituent atomic masses M'_a and M'_b ,

$$\mu' g_{\rm r}(R)' = \mu g_{\rm r}(R) - 2\kappa m_{\rm p} p(R) / (eR) + \kappa^2 m_{\rm p} Q \tag{4}$$

in which, in one of various forms [5],

$$\kappa = M'_{\rm a}/(M'_{\rm a} + M'_{\rm b}) - M_{\rm a}/(M_{\rm a} + M_{\rm b}).$$
⁽⁵⁾

3. Calculations

We undertook calculations of the rotational g factor and other molecular properties of H_2^+ , HeH⁺ and NeH⁺ as a function of internuclear distance with the computer programme Dalton 2.0 [8], using wavefunctions of complete active space self-consistent field (CASSCF) type with rotational London orbitals [9]. The conventional descriptions of the basis sets [10] are cc-pV5Z for NeH⁺ and aug-cc-pV6Z for both H⁺₂ and HeH⁺ as provided directly within Dalton 2.0. For both H_2^+ and HeH^+ , the large basis sets for both He and H and their contractions are, in standard notation, (11s6p5d4f3g2h|7s6p5d4f3g 2h), implying 262 atomic Gaussian functions contracted to 254; for Ne and H in NeH⁺, basis sets for Ne (14s8p4d3f2g1h|6s5p4d3f2g1h) and H (8s4p3d2f1g|5s4p3d2f1g) involved 166 atomic Gaussian functions contracted to 146. Such basis sets are known to converge in a consistent and predictable manner towards the basis set and theoretical limits. For HeH⁺ both the level of theory of these calculations and the number of orbitals in the active space— 8σ , 3π and 1δ —differ from those of our preceding calculation [2]. The active space of NeH⁺ comprised 6σ , 3π , 3δ and 1φ orbitals; in all cases the MP2 natural orbitals served as initial orbitals for the active space. The numbers of electrons in the active spaces were for H₂⁺ 1, HeH⁺ 2 and NeH⁺ 8. The quality of calculations for H_{2}^{+} and NeH⁺ was enhanced over published results. To derive the values of properties at $R_{\rm e}$, we conducted the calculations with optimization of geometry in one case for each species; in further calculations we fixed internuclear distances at values over a large range from nearly the united atomic ion to practically separate atom and ion. For the nuclear contribution to $g_r(R)$ we used formula (2) directly, with a nuclear mass derived from an atomic mass minus the appropriate number of electronic rest masses; the contribution of electronic binding energy to that calculation is negligible. For all calculations outside Dalton we used the most recent available values of atomic mass [11].

4. Results and discussion

Numerical values of quantities pertinent to rotational g factors for ${}^{1}H_{2}^{+}$, ${}^{4}He^{1}H^{+}$ and ${}^{20}Ne^{1}H^{+}$ appear in tables 1–3 respectively. Although we calculated values of g_{r} for these species in a few isotopic variants at various distances, we refrain from listing these values because they are reproduced quantitatively through the use of tabulated data and formula (4). In all cases the tabulated isotropic rotational g factor at each internuclear separation is a sum according to equation (1), with the electronic part taken as a further sum of separate diamagnetic and paramagnetic contributions that arise from the use of rotational London orbitals [9].

$$g_{\rm r}^{\rm el}(R) = g_{\rm r}^{\rm diam}(R) + g_{\rm r}^{\rm param}(R).$$
(6)

The tabulated values of g_r agree satisfactorily with those previously published [2, 3, 4, 12] with small discrepancies attributable to differences in basis sets and other minor variations in calculations, except that a systematic discrepancy with our previous values of $g_r(R)$ [2] reflects the incorrect calculation within Dalton 2.0 of the nuclear contributions that were incorrectly generated with atomic masses [2]. The differences between our values in table 2 and those calculated with a larger basis and greater extent of electronic correlation [2] are less than 0.003 at small distances and are negligible at larger distances. The accuracy of calculated values by comparison with values deduced from experiment is likely to be within 2% if results for many neutral molecules [13] might be taken as an indication applicable also to molecular ions. The characteristics typical of contributions to g_r apply to these diatomic molecular ions just as to neutral diatomic molecules [1]: $g_r^{nu}(R)$ is invariably positive, $g_r^{param}(R)$ is invariably negative, $g_r^{diam}(R)$ might be positive or negative, but $|g_r^{diam}(R)| < |g_r^{param}(R)|$ except when

Table 1. Rotational g factor of ${}^{1}\text{H}_{2}^{+}$ and its electronic contributions calculated as a function of internuclear distance^a.

$R/10^{-10}$ m	$g_{ m r}^{ m diam}$	$g_{ m r}^{ m param}$	gr
0.07	0.000 141	-0.000898	0.999 423
0.10	0.000047	-0.001559	0.998487
0.15	-0.000024	-0.003146	0.996 830
0.25	-0.000053	-0.007583	0.992 364
0.35	-0.000032	-0.013301	0.986667
0.45	-0.000020	-0.019959	0.980 021
0.55	-0.000013	-0.027392	0.972 595
0.65	-0.000012	-0.035524	0.964464
0.70	-0.000010	-0.039841	0.960 149
0.75	-0.000007	-0.044323	0.955671
0.85	0.000 001	-0.053775	0.946 226
0.95	0.000007	-0.063876	0.936131
1.00	0.000 009	-0.069170	0.930838
1.03	0.000 009	-0.072426	0.927 583
1.05	0.000 010	-0.074628	0.925 281
1.056 87 (R _e)	0.000 010	-0.075391	0.924618
1.08	0.000 010	-0.077982	0.922 028
1.10	0.000 011	-0.080251	0.919760
1.15	0.000 013	-0.086038	0.913975
1.25	0.000 023	-0.098070	0.901 953
1.35	0.000 044	-0.110836	0.889 208
1.45	0.000 081	-0.124212	0.875 869
1.55	0.000 135	-0.138213	0.861 922
1.65	0.000 207	-0.152805	0.847 389
1.75	0.000 294	-0.167936	0.832357
1.85	0.000 394	-0.183543	0.816851
1.95	0.000 508	-0.199548	0.800 960
2.05	0.000 636	-0.215858	0.784778
2.15	0.000772	-0.232362	0.768 410
2.25	0.000 906	-0.248936	0.751969
2.40	0.001 079	-0.273638	0.727 441
2.60	0.001 245	-0.305611	0.695 634
2.80	0.001 349	-0.335646	0.665702
3.00	0.001 409	-0.363010	0.638 399
3.50	0.001 453	-0.417300	0.584 153
4.00	0.001412	-0.452029	0.549 383
5.00	0.001 279	-0.483470	0.517809
6.00	0.001 177	-0.493234	0.507 943
7.00	0.001 130	-0.496659	0.504 470
8.00	0.001 106	-0.498 166	0.502 940
10.00	0.001 083	-0.499475	0.501 608
20.00	0.001 068	-0.500 629	0.500 438

^a $g_r^{nu} = 1.000\,000\,0146.$

both adopt small magnitudes at internuclear distances small or large relative to R_e . For H₂⁺, g_r^{diam} varies from -0.000052 to +0.001067 in a regular manner for values of R increasing through a large range in table 1; for the smallest values of R, g_r^{diam} has slightly positive values but these decrease with increasing R to a minimum near $R/10^{-10}$ m = 0.25 before increasing gradually and monotonically thereafter. For HeH⁺ the values of g_r^{diam} , all with small magnitudes <0.0003, seem to vary somewhat irregularly over a range $R/10^{-10}$ m from

Rotational g factors calculated for diatomic molecular cations H⁺₂, HeH⁺ and NeH⁺

Table 2. Properties of ${}^{4}\text{He}{}^{1}\text{H}^{+}$ —dipolar moment, diamagnetic and paramagnetic electronic contributions and total rotational *g* factor—calculated as a function of internuclear distance^a.

$R/10^{-10}$ m	$p/10^{-30} \mathrm{C} \mathrm{m}$	$g_{\rm r}^{\rm diam}$	$g_{ m r}^{ m param}$	gr
0.20	0.614 89	0.000 286	-0.035 907	0.864 521
0.30	1.145 56	0.000 217	-0.033459	0.866 901
0.40	1.842 50	0.000057	-0.033216	0.866 984
0.50	2.700 45	0.000 069	-0.034888	0.865 324
0.60	3.707 39	0.000 172	-0.037971	0.862 343
0.70	4.84832	-0.000010	-0.041908	0.858225
0.75	5.464 23	0.000 039	-0.044044	0.856 137
$0.774668~(R_e)$	5.78006	0.000 016	-0.045118	0.855 041
0.80	6.108 00	0.000004	-0.046227	0.853 920
0.85	6.777 80	-0.000044	-0.048423	0.851676
0.90	7.471 85	0.000 037	-0.050606	0.849 574
1.00	8.925 23	0.000071	-0.054882	0.845 331
1.10	10.45161	0.000 003	-0.059010	0.841 136
1.20	12.03172	0.000 028	-0.062998	0.837 173
1.30	13.644 07	-0.000006	-0.066858	0.833 278
1.40	15.26691	0.000027	-0.070577	0.829 592
1.50	16.88096	0.000 012	-0.074118	0.826 036
1.60	18.47163	0.000 031	-0.077430	0.822 744
1.70	20.02979	0.000 026	-0.080463	0.819705
1.80	21.551 58	0.000048	-0.083188	0.817 003
1.90	23.037 18	0.000 052	-0.085592	0.814 602
2.00	24.48942	0.000 062	-0.087683	0.812 521
2.20	27.31055	0.000 071	-0.091013	0.809 200
2.40	30.049 38	0.000080	-0.093424	0.806799
2.60	32.734 02	0.000 082	-0.095165	0.805 060
2.80	35.38367	0.000078	-0.096437	0.803784
3.00	38.01052	0.000079	-0.097380	0.802 841
3.50	44.52055	0.000075	-0.098868	0.801 350
4.00	50.987 12	0.000072	-0.099680	0.800 534
4.50	57.43141	0.000 069	-0.100165	0.800 046
5.00	63.86256	0.000 068	-0.100474	0.799736
7.00	89.52601	0.000 064	-0.101000	0.799 206
10.00	127.95760	0.000 062	$-0.101\ 197$	0.799007
20.00	255.97294	0.000 062	-0.101288	0.798917
40.00	511.96030	0.000 062	-0.101299	0.798 905

 $a g_r^{nu} = 0.900\,142\,52.$

0.4 to 1.7. The magnitudes of $g_r^{\text{diam}}(R)$ that we have calculated here for HeH⁺ are much smaller than those previously reported [2]; through test calculations in a series with *aug-cc*-*pVQZ*, *aug-cc-pV5Z* and *aug-cc-pV6Z*, we have verified that the values of $g_r^{\text{diam}}(R)$ decrease monotonically with increasing size of the basis set, consistent with the above observation. For NeH⁺ the behaviour of g_r^{diam} is more complicated but the variation is regular. The extent to which this behaviour reflects artefacts of the calculation is unclear, but in any case the generally small magnitudes have little effect on the total value of g_r .

The most notable features of our results for molecular ions are the limiting values of g_r towards the limits of a united atom and of separate atoms. For H₂⁺ and HeH⁺, g_r appears to tend to the corresponding value of g_r^{nu} as $R \to 0$, similar to the behaviour of H₂ [14]; a discontinuity must arise at R = 0 because for the united atom $g_r = 0$ identically. Although

Table 3. Properties of 20 Ne¹H⁺—dipolar moment, diamagnetic and paramagnetic electronic contributions and total rotational *g* factor—calculated as a function of internuclear distance^a.

$p/10^{-30}{ m C}{ m m}$	g_r^{diam}	$g_{\rm r}^{\rm param}$	gr
0.2453	0.002 988	-0.375420	0.603 770
0.485 1	0.001 958	-0.624925	0.353 234
0.7653	-0.001690	-0.834208	0.140 304
0.9100	-0.005195	-0.904829	0.066 177
1.0538	-0.006671	-0.951409	0.018 121
1.1944	-0.005594	-0.977468	-0.006861
1.3302	-0.003589	-0.985742	-0.013130
1.460 1	-0.001951	-0.978342	-0.004092
1.5832	-0.000964	-0.957670	0.017 586
1.6992	-0.000457	-0.926336	0.049 408
1.8601	-0.000146	-0.865234	0.110 821
2.006 1	-0.000050	-0.794148	0.182 003
2.0959	-0.000039	-0.744329	0.231 834
2.7954	-0.000311	-0.332672	0.643 218
3.401 8	-0.000512	-0.151972	0.823717
4.1020	-0.000708	-0.094402	0.881 091
4.9510	-0.000608	-0.084263	0.891 330
5.957 5	-0.000490	-0.089641	0.886070
7.1166	-0.000416	-0.097809	0.877977
8.4198	-0.000372	-0.103737	0.872 093
9.6857	-0.000364	-0.105646	0.870 192
11.423 5	-0.000365	-0.103317	0.872 520
13.1034	-0.000329	-0.097345	0.878 527
14.8830	-0.000235	-0.088768	0.887 198
16.7417	-0.000079	-0.078788	0.897 334
18.6552	0.000 135	-0.068531	0.907 805
22.5487	0.000 668	-0.050378	0.926 491
28.2669	0.001 345	-0.033429	0.944 118
37.0501	0.001 478	-0.024946	0.952733
45.1667	0.000 894	-0.023956	0.953 139
60.7273	0.000 360	-0.024043	0.952 518
76.0876	0.000 229	-0.024179	0.952252
106.6804	0.000212	-0.024311	0.952 102
152.4847	0.000212	-0.024364	0.952 049
305.0463	0.000213	-0.024389	0.952025
	$p/10^{-30}$ C m 0.2453 0.485 1 0.765 3 0.9100 1.053 8 1.194 4 1.330 2 1.460 1 1.583 2 1.699 2 1.860 1 2.006 1 2.095 9 2.795 4 3.401 8 4.102 0 4.9510 5.957 5 7.116 6 8.419 8 9.685 7 11.423 5 13.103 4 14.883 0 16.741 7 18.655 2 22.548 7 28.266 9 37.050 1 45.166 7 60.727 3 76.087 6 106.680 4 152.484 7 305.046 3	$p/10^{-30}$ C m g_r^{diam} 0.24530.002 9880.485 10.001 9580.765 3 $-0.001 690$ 0.9100 $-0.005 195$ 1.053 8 $-0.006 671$ 1.194 4 $-0.005 594$ 1.330 2 $-0.003 589$ 1.460 1 $-0.001 951$ 1.583 2 $-0.000 964$ 1.699 2 $-0.000 457$ 1.860 1 $-0.000 050$ 2.095 9 $-0.000 039$ 2.795 4 $-0.000 311$ 3.401 8 $-0.000 512$ 4.102 0 $-0.000 708$ 4.9510 $-0.000 608$ 5.957 5 $-0.000 490$ 7.116 6 $-0.000 372$ 9.685 7 $-0.000 364$ 11.423 5 $-0.000 364$ 11.423 5 $-0.000 365$ 13.103 4 $-0.000 235$ 16.741 7 $-0.000 079$ 18.655 2 $0.000 135$ 22.548 7 $0.000 668$ 28.266 9 $0.001 345$ 37.050 1 $0.001 478$ 45.166 7 $0.000 894$ 60.727 3 $0.000 360$ 76.087 6 $0.000 212$ 106.680 4 $0.000 213$	$p/10^{-30}$ C m g_r^{diam} g_r^{param} 0.24530.002 988 $-0.375 420$ 0.48510.001 958 $-0.624 925$ 0.7653 $-0.001 690$ $-0.834 208$ 0.9100 $-0.005 195$ $-0.904 829$ 1.0538 $-0.006 671$ $-0.951 409$ 1.1944 $-0.005 594$ $-0.977 468$ 1.3302 $-0.003 589$ $-0.985 742$ 1.4601 $-0.001 951$ $-0.978 342$ 1.5832 $-0.000 964$ $-0.957 670$ 1.6992 $-0.000 146$ $-0.865 234$ 2.0061 $-0.000 050$ $-0.794 148$ 2.0959 $-0.000 039$ $-0.744 329$ 2.7954 $-0.000 311$ $-0.332 672$ 3.4018 $-0.000 708$ $-0.094 402$ 4.9510 $-0.000 0372$ $-0.103 737$ 9.6857 $-0.000 364$ $-0.105 646$ 11.4235 $-0.000 365$ $-0.103 317$ 13.1034 $-0.000 329$ $-0.097 345$ 14.8830 $-0.000 325$ $-0.088 768$ 16.7417 $-0.000 079$ $-0.078 788$ 18.6552 $0.000 135$ $-0.088 768$ 16.7417 $-0.000 079$ $-0.078 788$ 18.6552 $0.000 135$ $-0.088 531$ 22.5487 $0.000 668$ $-0.050 378$ 28.2669 $0.001 345$ $-0.033 429$ 37.0501 $0.001 478$ $-0.024 946$ 45.1667 $0.000 229$ $-0.024 179$ 106.6804 $0.000 212$ $-0.024 364$ 305.0463 $0.000 213$ $-0.024 364$

^a $g_{\rm r}^{\rm nu} = 0.976\,200\,98$.

a classical rationale of this anomaly is readily deduced, a quantitative understanding of the calculation is lacking at present. Lack of convergence of the wavefunction at $R/10^{-10}$ m = 0.10 caused curtailment of calculations before that distance was attained. For NeH⁺ there seems to occur a resonance of some kind near $R/10^{-10}$ m = 0.13, at which point g_r exhibits a deep minimum \approx -0.014, before increasing again to a large value that might eventually attain g_r^{nu} ; because of problems with linear dependence of the basis functions when R approaches zero, the reliability of calculations of molecular electronic structure and properties at such small internuclear distances with standard conditions established for internuclear distances near those of chemical bonds is questionable. Tests of this behaviour with varied basis sets on both Ne and H demonstrated, however, that the observed minimum is not an artefact of a particular choice of basis set within reasonable limits.

A more interesting phenomenon occurs for large distances, corresponding to an approach to separate atomic entities. For neutral molecules such as H₂ [14] and LiH [15], $g_r \rightarrow 0$ as *R* becomes large, through a direct cancellation between electronic and nuclear contributions such that $g_r^{nu}(R) = -g_r^{el}(R)$. In contrast, for the three particular molecular ions treated here, g_r shows no such tendency, and its magnitude remains significantly greater than zero; that its sign is positive reflects the fact that a light and positively charged atomic ion—in each case here a proton or isotopic atomic nucleus of hydrogen—rotates about the centre of mass with a generally more massive neutral atom nearer that centre, as for neutral diatomic molecules [1]. A traditional interpretation [16] of the rotational g factor of electrically neutral diatomic species is that it measures the tendency of electrons to slip with respect to the rotating atomic nuclei. When the nuclei are far apart, i.e. for $R \gg R_e$, one expects each electron to be strongly associated with one or other nucleus so that slippage thus becomes negligible and $g_r \rightarrow 0$. Such an interpretation is clearly inapplicable for molecular ions: in no case here does the value of g_r approach zero at large R, in agreement with our previous results for HeH⁺ [2].

For X¹H⁺ with X = ¹H for ¹H₂⁺, X = ⁴He for ⁴He¹H⁺ and X = ²⁰Ne for ²⁰Ne¹H⁺, we find according to tables 1–3 that the limiting values, denoted by g_r^l , of g_r at large *R* approach closely in each case the ratio of the mass of atom X, M_X , and the total mass, M_t ; explicitly $g_r^l = M_X/M_t$ = 0.50, 0.80 and 0.952 for ¹H₂⁺, ⁴He¹H⁺ and ²⁰Ne¹H⁺ respectively. An explanation in terms of equation (3) would seem applicable, because for any molecular ion the electric dipolar moment, with respect to an origin at the centre of molecular mass, increases linearly with *R* in a range beyond significant interaction, other than purely electrostatic, between dissociating fragments. The second term of equation (3) hence becomes a constant for each isotopic species, with a magnitude equal to zero by symmetry of masses for ¹H₂⁺ but 0.082 54 for ²H¹H⁺, 0.5930 for ⁴He¹H⁺ and 0.8967 for ²⁰Ne¹H⁺. At a distance $R/10^{-10}$ m = 10.0, g_r^{irr} becomes 0.500 94 for ¹H₂⁺, 0.500 59 for ⁴He¹H⁺ and 0.500 78 for ²⁰Ne¹H⁺. Separate calculations for isotopic variants demonstrate that these values of g_r^{irr} are sensibly independent of isotopic masses for each separate compound.

For all three molecular ions treated in the present investigation, the path of dissociation of least energy yields $X + H^+$, with X being H, He or Ne as appropriate. Although the calculation of the static electric dipolar moment of ${}^{1}H_{2}^{+}$, or the dihydrogen molecular cation in another variant with like nuclear masses, yields a zero value, the dihydrogen molecular cation must dissociate unsymmetrically, into H + H⁺; such a breaking of symmetry must practically occur before an infinite internuclear separation, likely when that distance becomes a few times the equilibrium distance R_{e} . At any distance for $R \gg R_{e}$, the actual magnitude of the electric dipolar moment of such a molecular ion XH⁺ is simply a product of the elementary charge ewith the distance of H⁺ from the centre of mass of the system comprising a proton interacting weakly with a neutral atom; the latter is H, He or Ne for the molecules that we discuss here.

To provide a quantitative explanation of the limiting behaviour of g_r we have developed a new formula, based on formula (2) that was originally deduced for the nuclear contribution [5], and expressed in that context in terms of nuclear masses. For the limiting case in which $R \rightarrow \infty$, we consider the separate atoms as two classical point charges; rederiving formula (2) for this case yields this result,

$$g_{\rm r}(R) \to m_{\rm p}(Q_{\rm a}M_{\rm b}/M_{\rm a} + Q_{\rm b}M_{\rm a}/M_{\rm b})/(M_{\rm a} + M_{\rm b})$$
 (7)

in which Q_a and Q_b denote the net charges on the separating atoms. For a process AB⁺ \rightarrow A + B⁺, $Q_a = 0$ and $Q_b = +1$; accordingly this formula reduces to $g_r(R) \rightarrow m_p \mu M_b^{-2}$ in which M_a is an atomic mass and M_b is the mass of the atomic cation, which corresponds to the atom with the smaller ionization energy. Formula (7) is consistent with the case of a neutral diatomic molecule, for which $Q_a = Q_b = 0$, and conforms also to a classical model

Table 4. Rotational g factor calculated at $R = 10^{-9}$ m directly for each specified molecular ion, g_r from formula (7), distance d_{CM} of H⁺ from the centre of mass at $R = 10^{-9}$ m, and the quantity $g_r M_{\rm H} d_{\rm CM}^{-1}$.

Species	g_r^a	$m_{\rm p}\muM_{\rm b}{}^{-2\rm b}$	$d_{\rm CM}/10^{-10}{\rm m}$	$g_{\rm r} M_{\rm H} d_{\rm CM}^{-1} / 10^9$ u m ^c
³ He ¹ H ⁺	0.74975	0.74964	7.49640	1.0074
³ He ² H ⁺	0.30018	0.299 98	5.99658	1.0080
³ He ³ H ⁺	0.167 29	0.167 03	5.000 44	1.0088
⁴ He ¹ H ⁺	0.79900	0.798 94	7.98942	1.0073
⁴ He ² H ⁺	0.33294	0.33282	6.653 09	1.0076
⁴ He ³ H ⁺	0.19066	0.19051	5.703 25	1.0081
²⁰ Ne ¹ H ⁺	0.95205	0.95203	9.52034	1.0073
²⁰ Ne ² H ⁺	0.45451	0.45448	9.085 00	1.0074
²² Ne ² H ⁺	0.458 31	0.458 29	9.161 19	1.0073
$^{1}\mathrm{H}^{1}\mathrm{H}^{+}$	0.501 61	0.500 14	5.001 36	1.0102

^a Calculated directly with Dalton.

^b Calculated as $m_p M_a (M_a + M_b)^{-1} M_b^{-1}$ with protonic mass m_p , atomic mass M_a and atomic mass M_b of the separating cation.

^c Calculated with atomic mass M_b of the separating cation, which is ${}^{1}H^{+}$, ${}^{2}H^{+}$ or ${}^{3}H^{+}$.

of widely separated molecular ions in circular orbits. We present in the first column of table 4 numerical values of g_r that we calculated independently in each case at the same distance 10^{-9} m, although equation (4) equally well reproduces these values on the basis of a standard species for each compound; in the second column we derive values on the basis of this simple formula involving only values of atomic masses. According to the content of tables 1–3, $g_r(R)$ continues to decrease discernibly even for $R = 2 \times 10^{-9}$ m, but a convergent trend is evident. Comparison of values in columns 2 and 3 in table 4 shows that those values in column 2 are invariably larger than the corresponding values in column 3, consistent with the formula above constituting a limiting condition. The largest discrepancy between these corresponding values occurs for H_2^+ , for which table 1 shows the least rapid rate of convergence; this condition likely reflects the polarizable H atom reacting to the coulombic field of the separating hydrogen ion. Apart from the latter physical effect, the values in the first column are susceptible to small errors inherent in the calculation due to a finite basis set; the agreement between these two values of g_r is deemed satisfactory. This explanation moreover is consistent with an idea of slippage of electronic motion with respect to nuclear motion in neutral diatomic molecules [16]: tables 1–3 demonstrate that g_r approaches asymptotically its limiting value as $R \to \infty$ according to formula (7), that limiting value being zero for dissociation into neutral atoms.

According to an alternative point of view, the limiting value of g_r at large R might be related to the electric dipolar moment of the separating atoms. We found that a quantity formed from a quotient $g_r M_H/d_{CM}$, of which the numerator comprises a product of rotational g factor g_r at a large internuclear distance and the mass M_H of the particular separating hydrogen ion and the denominator is the distance d_{CM} of that hydrogen ion from the centre of mass, is essentially constant for a particular value of $R \gg R_e$ for all three compounds H_2^+ , HeH⁺ and NeH⁺ and for all their isotopic variants. Such a distance d_{CM} must be applied rather than electric moment because H_2^+ lacks the latter property. In columns in table 4 beside those of g_r appear the distance d_{CM} of the ion from the centre of mass based on an internuclear distance $R = 10^{-9}$ m and an assumption that the ion is H⁺ in one or other specified isotopic variants. In the case of ¹H¹H⁺, we assume dissociation into ¹H + ¹H⁺, although in our calculations the

5. Conclusion

We have derived a formula for the limiting value of the rotational g factor of diatomic molecular ions at large distances, which is not zero as for neutral diatomic molecules, and tested it against values for H₂⁺, HeH⁺ and NeH⁺ in various isotopic species. We also present accurately calculated values of $g_r(R)$ for these molecular cations over a large range from nearly the united atoms to nearly the separate atoms.

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