Energy levels of a polarizable linear polar molecule in a dc electric field obtained by analogy with the nonrelativistic hydrogen atom

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We note that an equation governing the dynamics of a polarizable linear polar molecule in a dc electric field coincides with one of two equations describing a hydrogen atom in the prolate spheroidal coordinate system. Using this analogy, as well as the known algebra of the angular momentum and Runge-Lenz-Pauli operators for the case of a hydrogen atom, the energy levels of a polarizable linear polar molecule in a dc electric field are calculated. For some cases, these energy values are exact.

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I. INTRODUCTION

The dynamics of a linear molecule possessing a permanent dipole moment in an electric field has been studied extensively since the inception of quantum mechanics (see, e.g., [1–5] and references cited therein). Difficulties that appear here are due to the fact that the corresponding Schrödinger equation does not reduce to an equation whose solutions can be expressed via standard and well-studied special functions such as, for example, the confluent hypergeometrical or Bessel functions. Hence, mainly numerical studies of the problem have been undertaken.

In this paper we would like to draw attention to one interesting analogy between this problem and "the most important" quantum-mechanics case, that is, the nonrelativistic Schrödinger equation for the hydrogen atom. This analogy enables us to express the energies of such a molecule via certain specific matrix elements obtained for the solution of the hydrogen atom problem; the characteristics of the latter are well known. In some cases, exact values of energy can be determined.

II. PROBLEM STATEMENT AND EXACT RESULTS

Let us write down Schrödinger equation for a polarizable linear molecule possessing dipole moment d, rotational constant B, and polarizabilities $\alpha_\parallel$ and $\alpha_\perp$ (these are the components parallel and perpendicular to the symmetry axis) in an electric field with strength F:

$$\left(BJ^2 - dF\cos\vartheta - \frac{1}{2}F^2(\alpha_\parallel\cos^2\vartheta + \alpha_\perp\sin^2\vartheta) - E\right)S_{n,m} = 0. \tag{1}$$

We can rewrite it in a somewhat different form:

$$\left(BJ^2 - dF\cos\vartheta - \frac{1}{2}F^2(\alpha_\parallel - \alpha_\perp)\cos^2\vartheta - \frac{1}{2}F^2\alpha_\perp - E\right)S_{n,m} = 0.$$

Expressing explicity the angular momentum square operator J^2 via $z=\cos\vartheta$ and dividing all terms by B, we obtain the following equation:

$$\left[\frac{d}{dz}\left((1-z^2)\frac{d}{dz}\right) - \frac{m^2}{1-z^2} + t_{n,m} + bz + a^2z^2\right]S_{n,m} = 0 \tag{2}$$

where $b=dF/B$, $a^2=(\alpha_\parallel-\alpha_\perp)F^2/2B$; $t_{n,m}=E/B+\alpha_\perp F^2/2B$, and thus $E=Bt_{n,m}-\alpha_\perp F^2/2$. Note that a^2 is positive because the inequality $\alpha_\parallel>\alpha_\perp$ holds for all linear molecules. If $b=0$ (which means that $d=0$) this equation is a prolate spheroidal wave equation whose main peculiarities are well known (see, e.g., [6]). In relation to molecular physics problems, this equation has been analyzed by Friedrich and Herschbach when discussing laser molecule traps [7]. It was also argued that the prolate spheroidal equation appears as a good approximation for some problems of the hydrogen atom in an external field, e.g., when discussing the simultaneous action of a Coulomb and a diamagnetic potential, or the linear Stark effect in a degenerate manifold [8–10].

The main topic of our paper is to exploit the following observation: for the general case when $d\neq 0$, Eq. (2) is equivalent to one of two equations appearing after the separation of variables for the Schrödinger equation describing an electron in the field of two Coulomb centers, having charges Z_1 and Z_2 and separated by a distance R, in prolate spheroidal coordinates (see, for example, [11] and references cited therein). In the usual notation $\xi=(r_1+r_2)/R$, $\eta=(r_1-r_2)/R$ (see Fig. 1) these equations read

$$\left[\frac{d}{d\eta}\left((1-\eta^2)\frac{d}{d\eta}\right) - \frac{m^2}{1-\eta^2} - \frac{1}{2}ER^2\eta^2 - R(Z_1-Z_2)\eta - Q\right]M_{n,m}(\eta) = 0, \tag{3}$$

$$\left[\frac{d}{d\xi}\left((\xi^2-1)\frac{d}{d\xi}\right) - \frac{m^2}{\xi^2-1} + \frac{1}{2}ER^2\xi^2 + R(Z_1+Z_2)\xi + Q\right]N_{n,m}(\xi) = 0. \tag{4}$$

Here Q is a separation constant. Note that in these equations E is an energy which for a bound system is essentially nega-

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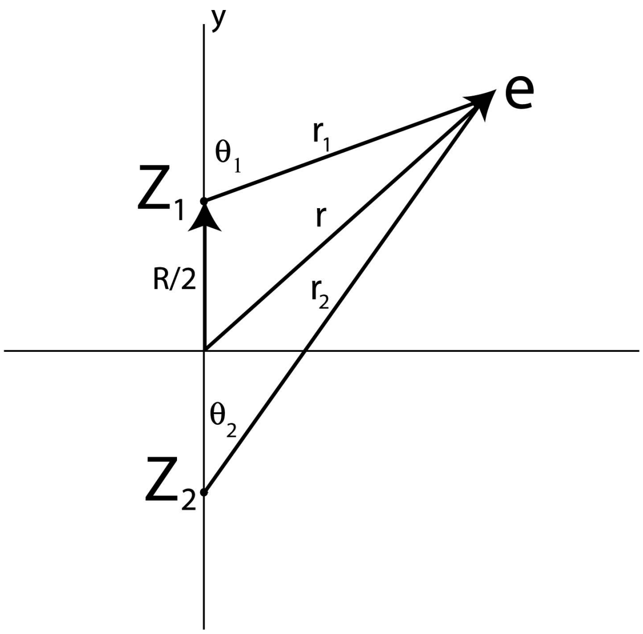

FIG. 1. Geometry of the problem.

tive. If we chose $Z_1=0$, $Z_2=1$ we will obtain the Schrödinger equation for the hydrogen atom, whose properties are well known.

Equation (2) coincides exactly with Eq. (3), describing the energy subspace $E=-1/(2n^2)$ of a hydrogen atom (here n is an integer), if one identifies

$$R = dF/B, \tag{5}$$

$$n^2 = d^2/[2(\alpha_\parallel - \alpha_\perp)B]. \tag{6}$$

Note that, contrary to the aforementioned appearance of the prolate spheroidal equation in some problems of hydrogen atom physics [8–10], this coincidence is exact. Here R is a standard parameter appearing for the linear polar molecule problem [1–5] which expresses the ratio between electrostatic and vibration energies. The condition for n to be an integer is easy to implement for plenty of real molecules: typically the value of $d^2/(2(\alpha_\parallel-\alpha_\perp)B)$ is large, and also neither d nor B nor $\alpha_\parallel, \alpha_\perp$ are known so precisely that difference between n obtained from (6) and the neighboring integer would be of great importance. For example, for the HCl molecule we have $d=1.109$ D, $B=10.59\text{ cm}^{-1}$, $\alpha_\parallel=2.6\times10^{-24}\text{ cm}^3$, $\alpha_\perp=1.625\times10^{-24}\text{ cm}^3$ [12] and thus $n^2=392.4$; $n=19.8$ and hence we can safely use the value $n=20$. Similarly, for HCN molecules we have $d=2.98$ D, $B=1.48\text{ cm}^{-1}$, $\alpha_\parallel=3.92\times10^{-24}\text{ cm}^3$, $\alpha_\perp=1.92\times10^{-24}\text{ cm}^3$ [12], hence $n^2=7500$ and the value $n=86$ or 87 can be taken. If desirable, this list can be made much longer (for example, very large values of n are obtained for molecules like NaCl, KI, etc.). Note also that the polarization energy $\cong\alpha F^2/2$ is negligible in comparison with the "orientation energy" dF provided $F\ll 2d/\alpha$, that is, for $d\cong0.1-1$ D, $\alpha\cong10^{-24}\text{ cm}^3$ up to very strong electric fields $F\cong10^7-10^8$ V/cm. In units of R and n this same ratio $\frac{1}{2}(\alpha_\parallel-\alpha_\perp)F^2/(dF)$ is equal to $R/(4n^2)$, which gives an appropriate "internal" scaling of the problem.

Of course, important differences between these two cases still persist. For a linear polar molecule we have only one Eq. (2) while two equations describe the dynamics of a hydrogen atom. This is the reason why the energy levels of a polar molecule can be determined for any value of a while for a hydrogen atom only those values of a that correspond to an integer n are permissible: only for such values is one able to find appropriate separation constants Q to obtain physically reasonable solutions for both equations. At the same time, for any a all values of $t_{m,n}$ that enable one to find a physically reasonable solution of (2) describe some energy state of a polar molecule.

This is of course valid also when n is an integer. However, for such a case the corresponding values of Q can be found using the well-developed quantum mechanics operator technique elaborated for the hydrogen atom case, and this is the aim of our study. Of course, we should note that not all values of energy can be determined by the identification at hand: obviously, there are an infinite number of energy states for any a while at most n^2 separation constants can appear for a given n. Nevertheless, for large enough values of n we can determine all energy levels of practical interest following this approach.

To proceed further we should recall that the eigenvalues of the separation parameter Q are the eigenvalues of the following operator giving an additional constant of motion [13–15]:

$$\Omega = -L^2 - \frac{R^2}{4}\left(\Delta - \frac{\partial^2}{\partial z^2}\right) - R(Z_1\cos\vartheta_1 - Z_2\cos\vartheta_2). \tag{7}$$

Here L^2 is the squared angular momentum operator and Δ is a Laplacian; see Fig. 1 for the designations. In the Appendix we show that for the hydrogen atom, when $Z_1=0$, $Z_2=1$, this operator reduces to the operator

$$\Omega_{at} = -L^2 + RA_z \tag{8}$$

where L^2 is the squared angular moment operator of the hydrogen atom and A_z is the z component of the Runge-Lenz-Pauli vector operator $A_i=0.5(\boldsymbol{p}\times\boldsymbol{L}+\boldsymbol{L}\times\boldsymbol{p})_i-r_i/r$; see, e.g., [16] for the further properties of this vector.

Thus to determine the spectrum of Q [which means to find the energy spectrum of a molecule in an electric field: the separation constant $-Q$ in Eq. (3) stands for the energy $t_{n,m}$ in Eq. (2)] we need to find the eigenvalues of the Ω_{at} operator. It is not very difficult to do because all matrix elements that appear when solving this problem are well known. For any given m we should consider the $(n-m)$-dimensional basis of orthogonal and normalized functions $\Psi_{nlm}=R_{nl}(r)Y_{lm}(\vartheta)e^{im\varphi}$, $m\leqslant l\leqslant n-1$, which is the solution of the hydrogen atom Schrödinger equation in a spherical coordinate system, and diagonalize the operator Ω_{at} in this basis. To do this we should write down expressions for the matrix elements for the terms forming the operator Ω_{at} in this basis. For L^2 it is well known that $\langle Y_{lm}|L^2|Y_{lm}\rangle=l(l+1)$; all other matrix elements are equal to zero. For determination of the values of matrix elements of the Lenz vector A_z we can use results given in [16], where it is shown that the corresponding nonzero matrix elements are

$$\langle \Psi_{l-1,m}|A_z|\Psi_{l,m}\rangle = C_l \frac{1}{n}(l^2-m^2)^{1/2},$$

$$\langle \Psi_{l+1,m}|A_z|\Psi_{l,m}\rangle = -C_{l+1}\frac{1}{n}[(l+1)^2-m^2]^{1/2}. \qquad (9)$$

Here $C_l = i[(n^2-l^2)/(4l^2-1)]^{1/2}$ if l is not equal to zero and $C_0=0$ [17].

Thus to find the eigenenergies of a molecule in an electric field one should diagonalize the following set of $(n\text{-}m)\times(n\text{-}m)$ quadratic matrices

$$\begin{pmatrix} -n(n-1) & i\frac{1}{n}R\left(\frac{n^2-(n-1)^2}{4(n-1)^2-1}\right)^{1/2}[(n-1)^2-m^2]^{1/2} & 0 & 0 \\ \text{H.c.} & -(n-1)(n-2) & i\frac{1}{n}R\left(\frac{n^2-(n-2)^2}{4(n-2)^2-1}\right)^{1/2}[(n-2)^2-m^2]^{1/2} & 0 \\ 0 & \text{H.c.} & -(n-2)(n-3) & \\ & & \vdots & \end{pmatrix}.$$

All these matrices are three-diagonal with little mixing of different L values. It is easy to see that values of energy obtained in such a way depend only on the absolute value of m and hence are at least doubly degenerate. This characteristic feature of a polar linear molecule is well known [1–5].

To obtain the energy values for the lowest states one should consider the case of small m ($m=0$ for the ground state, cf. [1–5]) and thus there are rather large matrices to diagonalize. This can be done only numerically, and we will present the corresponding results in the next section. Here we start with the case of large m. If $m=l=n-1$, we have only one possible value for the operator Ω_{at} and hence a single energy level of a linear rotor in an electric field: $E=Bn(n-1)-\frac{1}{2}\alpha_\perp F^2$. We should identify $n-1=J$ to recognize the familiar rotational energy of a molecule occupying the rotational level J, $E_{rot}=BJ(J+1)$, corrected for the polarization interaction with an electric field.

Surprising as it might seem, this value is *exact* [again, provided that the equality (6) holds exactly for some integer n and $J=m=n-1$]. The subspace spanned by the hydrogen atom eigenfunctions $\Psi_{nlm}=R_{nl}(r)Y_{lm}(\vartheta)e^{im\varphi}$, belonging to any concrete value of the principal quantum number n, is algebraically closed under the action of operators $\boldsymbol{L}$ and $\boldsymbol{A}$ [16] and hence no corrections from other energy subspaces can contribute to the value of the Ω_{at} operator. This remarkable result seems very difficult to obtain by other means. For example, if one tries to calculate the value of energy of a linear polarizable molecule in an electric field using the basis of pure rotational $|J,M\rangle$ levels, to obtain an exact value one will need to take into account an infinite series of contributions arising from all $|J',M\rangle$ ($J'\geqslant|M|$) levels (cf. [1–5]). It is difficult to imagine how this procedure can be fully completed. Nevertheless, as we see here, for the level $|J,\pm J\rangle$ and satisfaction of relation (6), an exact energy value is obtained.

The next set of exact energy levels can be obtained analytically when one considers the case of a 2×2 matrix appearing for $m=n-2$. Here one gets the following equation for the eigenvalues λ of the Ω_{at} operator:

$$\lambda^2+2(n-1)^2\lambda+n(n-1)^2(n-2)-R^2/n^2=0, \qquad (10)$$

which has the solutions

$$\lambda_{1,2}=-(n-1)^2\pm\sqrt{R^2/n^2+(n-1)^2}. \qquad (11)$$

For the case of small values of the saturation parameter dF/B, that is, when $R^2/n^2 \ll (n-1)^2$, we have $E=Bn(n-1)-\frac{1}{2}\alpha_\perp F^2+d^2F^2/(2Bn^2(n-1))$ and $E=B(n-1)(n-2)-\frac{1}{2}\alpha_\perp F^2-d^2F^2/(2Bn^2(n-1))$. Evidently, here we need to identify $J=n-1$ or $J=n-2$. Recalling also the definition (6), the term $d^2F^2/(2Bn^2(n-1))$ can be rewritten as $F^2(\alpha_{II}-\alpha_\perp)/J$, and we again can recognize the expression for the pure rotational energies of a molecule corrected by an orientation-averaged polarization interaction.

Finally, exact analytical solutions also can be presented for a 3×3 matrix corresponding to the case $m=n-3$ (see, e.g., [18] for details of the procedure for diagonalizing such matrices). We will not do this here, because using the Cardano formula to write down the solution of a cubic equation renders its practical application rather difficult. We proceed directly to presentation of numerical data.

III. NUMERICAL RESULTS

In Fig. 2 we present the results of numerical calculations (performed by diagonalization of 86×86, 85×85, and so on, matrices using a standard built-in option of the MATLAB package) concerning 15 low-lying energy levels (up to $J=4$) of a polarizable linear polar molecule. Energy is given in units of B. The value $n=86$ is used for the calculations, having in mind the HCN molecule; it has been tested that the calculation results are almost the same for a broad range of n exceeding 50 or so. In such a dimensionless form, these re-

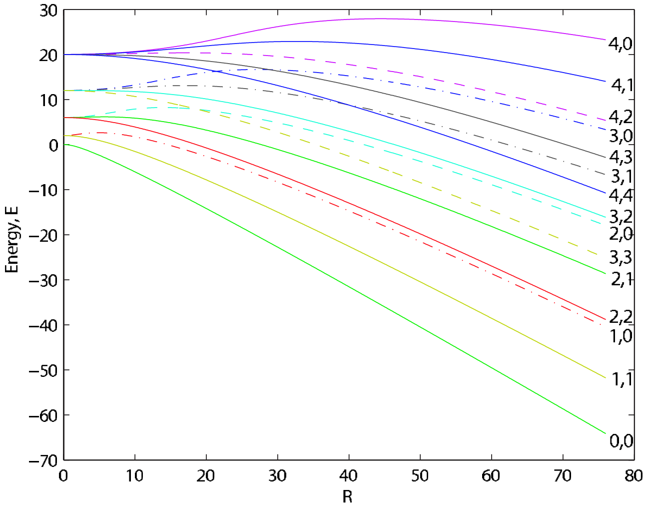

FIG. 2. (Color online) Dependence of a few low-lying energy levels E/B of a polarizable linear polar molecule in an electric field on the field strength $R=dF/B$. The case of $n=86$ is considered.

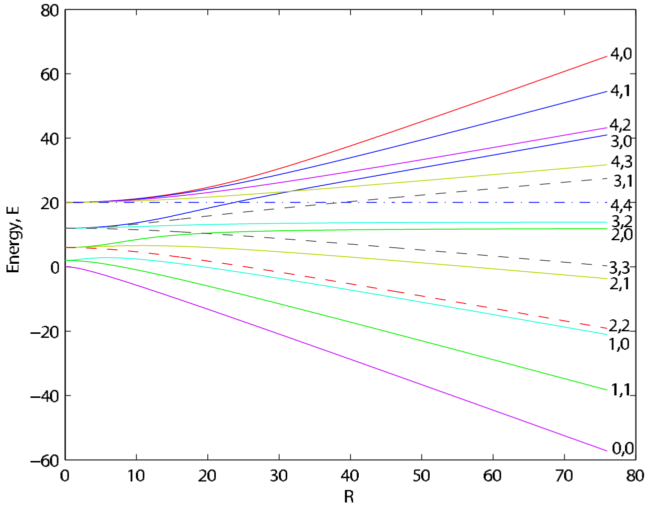

FIG. 3. (Color online) Dependence of energy levels E/B of a polarizable linear polar molecule in an electric field on the field strength $R=dF/B$. The case of $n=5$ is considered. For clarity, the value of $\alpha_{\perp}F^2/2B$ is not subtracted from the energy.

sults are quite suitable to compare with other calculations, and we deliberately show here the same picture as Fig. 1 of [1]: it is easy to see that these figures are virtually indistinguishable. This is not surprising because the inequality $R/(4n^2) \ll 1$ always holds here and hence the contribution of the molecule polarization to the energy is negligible. Thus Fig. 2 well attests the adequacy of this approach; in my opinion, the procedure of matrix diagonalization applied here is more straightforward and easier perform than the standard earlier approach to the problem (cf. [1–5]).

It is also instructive to look into the case when the value of n is small and hence the polarization interaction becomes important or even dominates the dipole orientation effect at reasonably large electric fields. (A similar case could have important implications for molecules or radicals like LiH, BeB, etc., which are characterized by a relatively small dipole moment, large rotational constant, and large polarizability; these practical implications will be considered elsewhere). In Fig. 3 we present data obtained for such a case with $n=5$. An essentially different energy-level picture appears here. It is worthwhile to note that, in view of the aforementioned appearance of the prolate spheroidal equation when solving the problem of the hydrogen atom in external electric and magnetic fields [8–10], Figs. 2 and 3 have certain connections with the mapping of Stark levels in strong magnetic fields (see, e.g., [19]).

IV. CONCLUSIONS

In this paper the energy levels of a polarizable linear polar molecule in an electric field are calculated using an analogy between this problem and the problem of a hydrogen atom in a prolate spheroidal coordinate system. In some cases, exact values of energy levels can be obtained, which makes the consideration especially interesting. In our opinion, apart from the practical interest, this result once again reveals fruitful analogies appearing throughout quantum mechanics between its different branches as well as the usefulness of the Schrödinger equation for the hydrogen atom.

APPENDIX

Let us start from the expression (7) for the operator Ω which has been derived earlier [13–15]:

$$\Omega = -L^2 - \frac{R^2}{4}\left(\Delta - \frac{\partial^2}{\partial z^2}\right) - R(Z_1 \cos \vartheta_1 - Z_2 \cos \vartheta_2). \tag{A1}$$

The operator L^2 is the square of the $\boldsymbol{L}=\boldsymbol{r}\times\boldsymbol{p}$ operator. We can substitute for the vector $\boldsymbol{r}$ the value $\boldsymbol{r}_2-\boldsymbol{R}/2$ (see Fig. 1) and thus get for L^2 the following expression:

$$L^2 = (\boldsymbol{r}_2 \times \boldsymbol{p})^2 - 0.5[(\boldsymbol{r}_2 \times \boldsymbol{p})(\boldsymbol{R} \times \boldsymbol{p}) + (\boldsymbol{R} \times \boldsymbol{p})(\boldsymbol{r}_2 \times \boldsymbol{p})] + 0.25(\boldsymbol{R} \times \boldsymbol{p})^2. \tag{A2}$$

For the case when we have only one nucleus located at the point O' with a radius vector $-\boldsymbol{R}/2$ (the hydrogen atom case: $Z_1=0$, $Z_2=1$) we can identify $\boldsymbol{r}_2\times\boldsymbol{p}$ with the L_{at} operator for this hydrogen atom. Note that $0.25(\boldsymbol{R}\times\boldsymbol{p})^2$ is equal to $-\frac{R^2}{4}(\partial^2/\partial x^2+\partial^2/\partial y^2)=-\frac{R^2}{4}(\Delta-\partial^2/\partial z^2)$; hence the corresponding term in (A1) is canceled out and we have

$$\Omega = -\boldsymbol{L}_{at}^2 + 0.5[\boldsymbol{L}_{at}(\boldsymbol{R} \times \boldsymbol{p}) + (\boldsymbol{R} \times \boldsymbol{p})\boldsymbol{L}_{at}] + R \cos \vartheta_2. \tag{A3}$$

Now let us change the origin of the coordinate system to the position of location of the nucleus of this atom (point Z_2 in Fig. 1). Evidently, $R \cos \vartheta_2$ is equal to Rr_z/r, where r is the electron coordinate in this new coordinate system. From elementary vector algebra it follows that the expression in square brackets in (A2) is equal to R times the z projection of a vector $0.5(\boldsymbol{p}\times\boldsymbol{L}+\boldsymbol{L}\times\boldsymbol{p})$ and hence, recalling the definition of the Runge-Lenz-Pauli operator $A_i=0.5(\boldsymbol{p}\times\boldsymbol{L}+\boldsymbol{L}\times\boldsymbol{p})_i$

$-r_i/r$ [15], one gets the equation used in the text:

$$\Omega_{at} = -L^2 + RA_z. \tag{A4}$$

Note that use of the spherical coordinate system corresponds to a description of the hydrogen atom when the L^2 and L_z operators have certain definite values. The Parabolic coordinate system corresponds to description when the L_z and A_z operators have definite values. The prolate spheroidal coordinate system corresponds to the case where neither L^2 nor A_z has definite values but their linear combination $L^2 - RA_z$, where R is an arbitrary parameter, has. (Another operator having definite values is, of course, again L_z.)

For the case when one chooses $Z_2=0$ instead of $Z_1=0$, one gets the opposite sign in (A4), $\Omega_{at}=-L^2-RA_z$, and for this case the linear combination L^2+RA_z has definite values.

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